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DEVELOPMENT OF AN APPROACH TO IDENTIFICATION OF EMERGING TECHNOLOGY AND DEMONSTRATION OPPORTUNITIES

Battelle Columbus Laboratories

PREPARED FOR
Environmental Protection Agency

May 1974

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The report gives results of a study to develop methodology for characterizing major industries from the standpoint of their present environmental impact and for assessing the probable effect of emerging process technology on environmental considerations. It describes a systematic method for separating the industries into process modules. It demonstrates the applicability of this approach, using as examples the petroleum refining and secondary nonferrous metals industries, each with substantially different characteristics. It also reports an approach utilizing expert opinion for rapid identification of emerging technology, and discusses technology being developed in the two industries.

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PROCESS DESCRIPTION OF THE ZIRCONIUM SEGMENT OF THE SECONDARY NONFERROUS METALS INDUSTRY

There are two zirconium processors in the United States. Most of their product is used in nuclear reactors in the civil and military applications.

The scrap zirconium market is very small. In fact, the two processors do not, as a rule, purchase any scrap except those routinely generated in their regular customer operations. This state prevails because scrap from unknown sources makes the control of product quality very difficult.

Production volume of zirconium (primary and secondary) is a proprietary secret. Estimates, however, range from 3 to 5 million pounds. The product sells at about 10 to 15 dollars per pound.

As in the case of indium, hafnium, and beryllium, currently employed product process details are not available. However, since the total market is very small and the product is very expensive, the processors are economically constrained to maximize recovery. This insures low ambient or indoor emissions of zirconium.

Zirconium is not a toxic material.

U. S. producers of zirconium do not seem to be interested in outside help in their research and development activities. This trend may not change in the foreseeable future.

Population of Secondary Zirconium Processors

(1) Amax Specialty Metals Division
American Metal Climax, Inc.
6000 Hake Road
Akron, New York 14001
Telephone: (716) 542-5454

(2) Teledyne Wha Chang
P. O. Box 460-T
Albany, Oregon

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by

H. Nack, K. Murthy, E. Stambaugh, H. Carlton, and G.R. Smithson, Jr.

Battelle--Columbus Laboratories
505 King Avenue,
Columbus, Ohio 43201

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Control Systems Laboratory
National Environmental Research Center
Research Triangle Park, North Carolina 27711

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I. ABSTRACT

Results of a study to develop methodology for characterizing major industries from the standpoint of their present environmental impact and assessing the probable effect of emerging process technology on environmental considerations are discussed. A systematic method for separating the industries into process modules is described and illustrated. Applicability of this approach is demonstrated, using the petroleum refining and secondary nonferrous metals industries as examples. These are two industries with substantially different characteristics. An approach utilizing expert opinion for rapid identification of emerging technology is also reported and a discussion of technology under development in the two industries is presented.

II./ INTRODUCTION

The objectives of the study were to develop an approach to the assessment of the environmental effects associated with industrial activities and identification of new process technology which could be employed to minimize adverse environmental effects. The approaches developed were intended to be suitable for rapid assessment of major industries so that EPA could assess the future need for demonstration programs similar to those used to promote the use of newly developed technology to the electric utilities and by the iron and steel industry.

The petroleum refining industry and secondary nonferrous metals industry were selected for evaluation in a pilot program. The differences in the character of these two industries would help identify all pertinent factors in a methodology which would be applicable, with little or no modification, to any industry or interest.

Phase I of the study was concerned with development of industrial process profiles for each industry. The profiles are included as Appendix B (Refining) and Appendix C (Nonferrous Metals). The companies of importance, the raw materials used, processes employed, and the products and wastes were identified. Standard terminology under development by EPA's Control Systems Laboratory for similar studies was employed, and is included as Appendix A. The industry profiles were developed from information obtained from the literature available within Battelle and by telephone contacts with industries. After assembling readily available information, a list of practicing industry experts was developed for Phase II.

Phase II of the study consisted of consulting with the experts from the two industries to verify the accuracy and completeness of the profiles and to identify technological trends and developments germane to the project. The input by the experts to the profiles and to the identification of environmental problem areas that have received recent technological solutions was considerable.

In Phase III information on emerging technology* was assessed and candidate demonstration projects were identified. Projects were considered primarily from the standpoint of their potential for achieving a significant reduction in air pollution. The feasibility of setting up a jointly-sponsored government-industry project was also examined.

In Phase IV experience gathered during the course of the study was reviewed by participating staff as the basis for preparation of this report. Here the experience in applying the identification approach to the petroleum refining and the secondary non-ferrous metals industries were assessed.

It is anticipated that the information developed in this study coupled with EPA's broad knowledge of air pollution control needs can be used to select candidate demonstration projects. Pursuing selected candidate projects to obtain defined end results could be done by the EPA either alone or in concert with a contractor mutually acceptable to both the EPA and the candidate company. It is also anticipated that the techniques developed here will assist in similar assessment work of other industries.

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* The term "emerging technology" connotes technology in a developmental state that has a good potential for commercialization and significantly helps to abate existing environmental problems in the industry. The technology may include a new process, a process modification, or an improved emission control technique or a combination of these.

III. DESCRIPTION OF THE APPROACH

The approach to identification of the emerging technology* was comprised of the various tasks indicated in Figure III-1 completed in four phases and in four time frames. As indicated in Figure III-1, some of the tasks in each of the phases are accomplished concurrently. The tasks in each phase are defined as follows.

Phase I. (1) Gather available in-house process data
(2) Obtain available process data from industry by telephone contacts. Also concurrently establish industry contacts
(3) Incorporate the above data along with prior in-house experience into generation of industry process profiles (See Appendix C)

Phase II. (4) Concurrent with Tasks (1) and (2) of Phase I conduct preliminary selection of experts from industry and private consultation firms
(5) Coincident with the completion of Task (3) of Phase I, select final list of experts
(6) Have the industry process profiles reviewed by the experts of the industry

Phase III. (7) Finalize the industry process profiles after incorporating additions, changes and other comments from the experts
(8) With expert opinion, complete the precise definition of environmental problems
(9) List and elaborate on the identified emerging technology* in each industry

Phase IV. (10) Prepare final report of the results of the approach. Make appropriate recommendations.

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* See definition on Page II-2 (footnote).

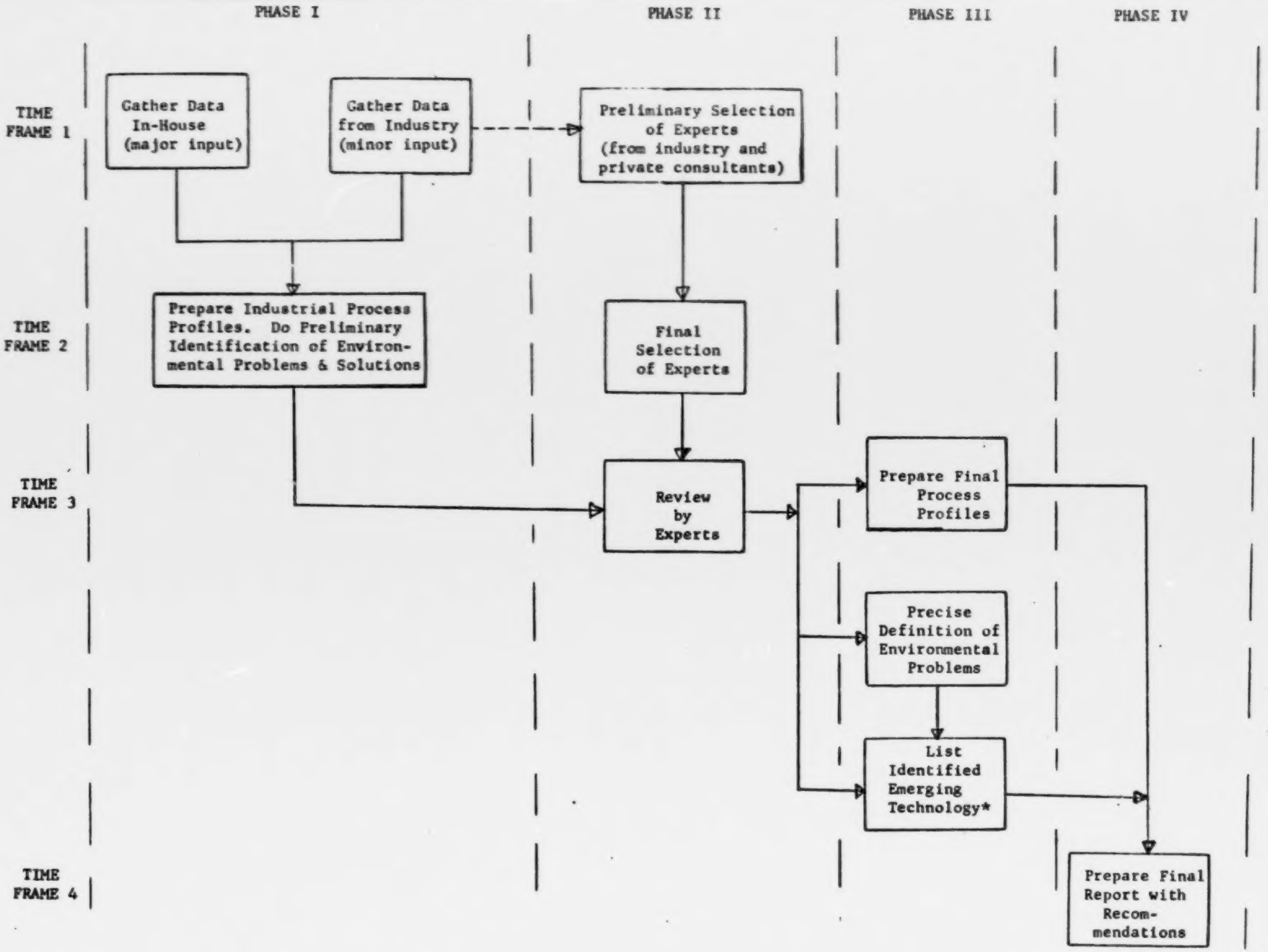
PHASE I
PHASE II
PHASE III
PHASE IV
TIME FRAME 1
TIME FRAME 2
TIME FRAME 3
TIME FRAME 4
Gather Data In-House (major input)
Gather Data from Industry (minor input)
Preliminary Selection of Experts (from industry and private consultants)
Prepare Industrial Process Profiles. Do Preliminary Identification of Environmental Problems & Solutions
Final Selection of Experts
Review by Experts
Prepare Final Process Profiles
Precise Definition of Environmental Problems
List Identified Emerging Technology*
Prepare Final Report with Recommendations

FIGURE III-1. SCHEMATIC OF APPROACH TO IDENTIFICATION OF EMERGING TECHNOLOGY*

* The term "emerging technology" connotes technology in a developmental state that has a good potential for commercialization and significantly helps to abate existing environmental problems in the industry. The technology may include a new process, a process modification, or an improved emission control technique or a combination of these.

The approach described above while enabling an orderly performance of the tasks also permits planned contact with the most knowledgeable persons in the area under study.

Steps in Preparation of Industrial Process Profile

The secondary nonferrous metals industry is highly fragmented from the standpoint of processes employed, has a multiplicity of products, utilizes numerous raw materials and produces a wide variety of potential air pollutants. In all, the industry encompasses some 20 different segments, (comprising a total of 135 processes) each of which is unique in regard to raw materials sources, products produced, processes employed and pollution potential. Therefore, each segment had to be treated separately. The petroleum refining industry, more standardized from the standpoint of technology employed, was reducable to 29 processes.

In developing the industrial process profile for secondary nonferrous smelting, the first task entailed the development of industry segment profiles. This involved initially, the use of the literature and Battelle personnel to develop flowsheets and process descriptions. Each flowsheet identified:

(1) The manufacturing operations
(2) The processes within each operation
(3) The processing steps within each process
(4) Raw materials, source of energy, etc., used in each process
(5) Types of potential pollutants--atmospheric emissions, aqueous waste, and solid waste
(6) Intermediate products and final products.

The flowsheets were then used as guides around which to build the process descriptions. A similar approach was used for petroleum refining.

In addition to discussing the above items, composition of emissions, seriousness of the atmospheric pollution problems, and disposal of the waste materials were taken into consideration and the pollution potential of the present processes were defined. For this task standard nomenclature and techniques developed by the Control Systems Laboratory for industry analysis were used. The nomenclature definitions are shown in Appendix A. Having completed this task, the next task involved the identification of emerging technology and obtaining expert opinion on validity of the flowsheets and process descriptions.

Selection of Experts*

Because of the complexity of the secondary nonferrous metals industry, the selection of two or three experts to cover the entire industry was not possible. Instead, it was necessary to select experts in the specific segments of the industry. Initial selection of experts was made based on recommendations from management officials in the major companies. The experts suggested were then interviewed by telephone and, if found technically qualified for the task, were enlisted to provide assistance on this project.

The petroleum refining industry, being more systematized, required discussion with fewer experts.** Those used were selected to provide a cross section of opinion; i.e., one was employed by a major petroleum company, two were employed by a major engineering company, one was a private consultant and one was a Battelle in-house expert.

Identification of Emerging Technology***

First, a preliminary initial identification of emerging technology was done by the use of current literature and Battelle's in-house expertise. Next, experts in the two industries of interest and government agencies such as the U. S. Bureau of Mines were contacted by telephone and/or personal visits to:

(1) Identify additional emerging technology

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* See Appendix A (Page A-4) for list of experts contacted.

** See Appendix A (Page A-3) for list of experts contacted.

*** See definition on Page II-2.

(2) Obtain their opinion on the previously identified emerging technology

(3) Obtain comments on the accuracy and thoroughness of the process descriptions and flowsheets of the various segments and make corrections where necessary.

In arranging visits, the normal procedure was to contact a company by telephone at least 3 weeks prior to any visit to request assistance on the subject. If agreeable, as was the case in most instances, a package including a process flowsheet, process description, and brief write-ups on emerging technology was mailed at least one or two weeks prior to the visit. Many companies requested time to allow several individuals to review the data.

During the visit (which was made generally by two BCL personnel), the process descriptions and flowsheets were reviewed first, followed by review of the emerging technology that BCL staff had identified. Then efforts were made to identify additional emerging technology in terms of air pollution control approaches, future trends in processing, and also obtain atmospheric emissions data. Information on candidate companies who would be interested in jointly funded demonstration studies was sought.

Also, efforts were made to determine the attitude of the company toward such matters as demonstrations with government support, type of support most beneficial to the secondary industry, and technical capabilities of the company. The results of the efforts are described in appropriate Sections on pages V-2, V-3, C-1 and C-2.

Simultaneously, the same packages were being reviewed by outside consultants and the same questions were being posed to them. Conferences also were being held with consultants at BCL as well as in the field.

IV. AIR POLLUTION PROBLEMS AND DEMONSTRATION OPPORTUNITIES

Secondary Nonferrous Metals Industry

The secondary nonferrous metals industry presents a wide variety of air pollution problems associated mostly with pyrometallurgical processes used for smelting, refining, and burn-off of foreign materials. Some of the most important problems and specific solutions of interest are discussed below.

Burning of Insulation and Other Organics from Copper Scrap in the Copper Segment

Problems encountered are: (a) toxicity and corrosive nature of the gases due to the halogen, sulfur, and heavy metals content, (b) high concentration of unburned organic materials, and (c) the loss of metal values contained in the atmospheric emissions. Efforts to control these emissions have had limited success. New or improved technology is needed.

Specific solutions toward controlling atmospheric emissions being tried are:

(1) The U. S. Metals Refining Company of Carteret, New Jersey, is using a reactant-coated baghouse to collect HCl and other halides which are liberated when copper wire is burned to remove insulation.

(2) The Apex Smelting Company of Chicago, Illinois, is installing a chemically coated baghouse at its aluminum smelter in Cleveland, Ohio, to collect chlorides from the demagging operation.

Removal of Organics, Such as Cutting Oils, from Scrap Turnings, Shavings, and Borings, as in the Brass and Bronze Segment

Problems encountered are: (a) high incidence of fires in the baghouses, (b) heavy emissions of zinc oxide and other metallic fumes, and (c) severe fire hazard during the charging of the scrap to the melting pot.

These problems are encountered in the Brass and Bronze Segment and the Copper and Aluminum Segments.

One specific solution to the problem of fire in baghouses in current use is described below.

The ABC* Company of XYZ* City is injecting a fine powder into the off gases from the brass and bronze melting furnaces. This fine powder reduces the incidence of fires in the baghouses, apparently by reaction with the fumes, dusts, and/or gases to form products which do not ignite as readily as the original material. Other companies are de-oiling the scrap before melt-down by burning to reduce chances of fire. The ABC Company claims that de-oiling is not necessary.

Sulfur Oxide Emissions from Melting of Battery Plate Scrap in the Lead Segment

Battery plate scrap is contaminated with residual sulfuric acid. Failure to remove the acid prior to melting results in evolution of sulfur oxides. The SO_x emissions vary, being high during initial melt-down and low at the end of the processing stage.

This is a major problem in the Lead Segment; the Copper Segment faces similar problems.

Solutions being tried for the abatement of SO_x emission from Lead Segment are:

(1) Lime-sulfur dioxide scrubbing system at the General Battery Corporation, Reading, Pennsylvania. This system uses wet scrubbing with hydrated lime. The underflow sludge, the flyash resulting from burning pulverized coal and the crushed plastic battery cases are being tried to produce a composition that is sanitary, nonreverting, nonleaching and dimensionally stable.

The process was developed by G & W.H. Corson Inc., Plymouth Meeting, Pennsylvania. The Company is not desirous of EPA assistance in the project.

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[*] Names and identity are deliberately withheld, as requested.

(2) The U. S. Bureau of Mines in College Park, Maryland, is developing a process for reducing the sulfur oxide emissions from recovery of lead from scrap battery plates. This process entails:

- (a) Heating a mixture of the lead scrap and calcium hydroxide in a calciner to convert the sulfur content to calcium sulfate
- (b) Adding solid reducing agent and flux and reducing the charge at 650°C which is below the decomposition temperature of calcium sulfate
- (c) Removing molten lead for further processing and the slag for disposal. Consideration is being devoted to developing a process for the regeneration of the calcium sulfate to lime for recycle and generation of elemental sulfur for use in other processes.

Collection and Utilization of Fumes and Dusts from Smelting and Refining Operations and Disposal of Heavy Metal Sludges from Wet Scrubbers

Problems encountered are: (a) collection of fine dust particles (less than 0.5 micron in diameter), (b) loss of valuable metals, (c) high level emissions to the atmosphere from current pyrometallurgical processes, and (d) disposal of dusts and fumes collected in baghouse in landfills which could result in severe water pollution problems and possibly air pollution problems.

Wet scrubber sludges resulting from control of atmospheric emissions contain metal values too dilute to render its recovery economical. Again, these sludges are disposed off in landfills, thus making water pollution problems a possibility.

The melt-down of scrap fines together with coarse scrap in many segments results in heavy evolution of metallic dusts and fumes. To avoid this problem, some companies dispose of the scrap fines in landfills rather than recover the metal value in it. The result could be a water pollution problem from the leachates.

The above problems are being solved by the industry by multiple approaches. Examples are provided below.

Development of New Processes. (1) Hydrometallurgical systems are being examined as a means of reducing atmospheric emissions by eliminating the pyrometallurgical step in the recovery process. For example, Electrolytic Zinc Company of Australia, Limited, has developed a new hydrometallurgical process for extracting lead from zinc plant residues using aqueous solutions containing ammonia and ammonium sulfate to dissolve lead compounds insoluble in conventional solvents. The Bureau of Mines, Salt Lake City Metallurgy Research Center, Salt Lake City, Utah, has developed a process for the recovery of copper for all grades of scrap copper using an ammonium carbonate system. Essentially, no atmospheric emissions are generated and aqueous solutions can be regenerated and recycled. The copper can be recovered as the powder, oxide, or as cathodic copper.

(2) U. S. Metals Refining Company (Division of AMAX) at Carteret, New Jersey, is developing a hydrometallurgical process for the recovery of metal values from dust and fumes collected as baghouse dusts from the various segments of the primary and secondary industries. The process has been developed through the laboratory stage and is now ready for pilot-plant development.

Basically, the process entails the extraction of metal values from the baghouse dusts with an aqueous leachant to produce a metal-laden liquor. The metal values, such as zinc, are then recovered from this liquor by an electrolytic process. In those instances where the dusts contain high concentrations of iron values, the leach residue after removal of the nonferrous metal values is returned to the steel industry for processing in the blast furnaces. Other metals such as lead and tin are recovered at various stages in the process.

While this process does not treat the air pollution problem from the secondary nonferrous metals industry per se, it does eliminate or reduce a potentially serious water pollution problem which could arise upon disposal of the dusts and sludges by landfilling. Furthermore, the process recovers valuable metals which would not otherwise be recovered.

(3) Zinc dust manufacture is rapidly growing in the Zinc Segment. One new process which has been introduced into this country is a Norwegian process known as the Larvic process. In this process, the zinc is vaporized using graphite rod resistors above the melt contained in a reverberatory furnace. Consequently, emissions are minimized as there are no combustion gases. Currently, the process is being used by The American Smelting and Refining Company, in New Jersey. This process is in contrast to the pyrometallurgical processes for zinc powder manufacture used in the U. S. Although theoretically hydrometallurgical processes can be used for making zinc powder, there is no evidence of its use in the U. S.

(4) Battelle's Columbus Laboratories, Columbus, Ohio, is developing a process for fluxless melting of magnesium. The process is designed to use small percentages of hexafluoride in air as a protective atmosphere for molten magnesium in various molten metal handling operations. Successful development of this process will: eliminate or minimize the use of flux when melting magnesium; result in reduced air pollution problems associated with the flux; reduce the solid wastes generated; and produce cleaner castings. Currently, the process is in the laboratory stage of development.

Modification of Current Processes. Oxygen-enriched air or in some cases pure oxygen is being used in a number of industry segments, e.g., Copper, Lead, and Aluminum. Advantages are reduced volume of off-gases, increased production capacity, and low emission of dusts and fumes per ton of metal produced. Two companies currently using oxygen or enriched air are Franklin Smelting Company of Philadelphia, Pennsylvania, and Chemical Metals Corporation, East Alton, Illinois. Franklin Smelting Company has developed a rotary converter for the production of black copper. Emissions should be significantly reduced over conventional converters as surface lancing in place of tuyerers is used and pure oxygen is used in place of air. Chemical Metals Corporation is using enriched air overhead converters.

Halide Evolution from Aluminum Segment

Demagging of aluminum with gaseous chlorine results in the evolution of large quantities of chlorine, primarily as aluminum chloride. The use of solid demagging agents such as aluminum fluoride or aluminum chloride instead of chlorine reduces the degree of severity of the problem and is being practiced by the industry. A new approach involves the use of a precoated baghouse (chromatographic baghouse) which removes both the halides and particulate matter. This technique is being tested on a commercial in Canada, and several U. S. Companies are contemplating building commercial-size units.

Pollution from Aluminum Drosses

Drosses from the Aluminum Segment consist of aluminum, sodium, and potassium chlorides, fluxes, etc. These react with atmospheric nitrogen and water to form ammonia, an atmospheric pollutant. The quantity of drosses is significant and solution to the problem is not attempted in the U. S. yet.

It appears that the European industry has a process to recover the aluminum from the drosses and recycle the salts and fluxes. The specific details of this technology are not known at this time.

Demonstration Opportunities

Any of the solutions described above can be a potential candidate for a demonstration project. However, exact definition of the solution being tried and the willingness of the developers to cooperate in a demonstration project with EPA needs detailed investigations. As noted above, many of the developers are unwilling to invite the EPA.

Some of the companies might welcome cooperation and support by EPA through a mutually acceptable contractor or coordinator. The secondary nonferrous metals industry is primarily production oriented and the suspicion that EPA intervention might hinder their normal production activities appears to have put the industry on guard.

Further work in this direction to more clearly identify demonstration projects and companies willing to cooperate is worthwhile.

Petroleum Refining Industry

Petroleum refineries have four air pollution related problems: (1) particulate and SO_2 emissions from the Cat-Cracker Catalyst Regenerator, (2) emission of sulfur oxides in tail gases from Claus plants, (3) emissions from fuel combustion in the industry and (4) Disposal of high-sulfur residue fuels.

Catalytic Cracker

Catalytic cracker regenerator flue gases contain particulates and at times significant quantities of sulfur oxides. Electrostatic precipitators are most commonly employed to remove particulates; sulfur oxides are not normally controlled. Exxon plans to install a full-scale (size) scrubber that employs a soda ash solution for removal of both pollutants. The unit is expected to produce data needed for design of future units. Evaluation of the effectiveness of this unit may be useful if sulfur oxides from cat cracking will require more effective control in the future.

Claus Plant

A number of processes designed specifically for Claus plants are being introduced for more effective control of sulfur emissions in the tail gas. These include Shell's Scot process, Union Oil's Beavon process, the Cleanair process offered by J. F. Pritchard, the IFP process developed by Institut Francais du Petrole, Lurgi's Sulfreen process and the Takahax process licensed by Kellogg. In addition, the Wellman-Lord process and the citrate process are being offered for tail gas scrubbing. A demonstration or evaluation of one or all of these processes would be appropriate if EPA considers the development of data on the economics of control useful. Such information would be useful in defining the control alternatives open to refineries as they replace dwindling supplies of sweet crude with available high-sulfur crude.

Disposal of High Sulfur Resids

Refining capacity in the U. S. is being expanded and more high-sulfur crudes are being refined. Therefore, supplies of high-sulfur resid will increase and processes for its utilization in economical environmentally sound ways will be increasingly useful. A process that could be used to convert resid into a nonpolluting fuel would be especially attractive. Two possible processes for such service are the Chemically Active Fluid Bed and Exxon's Flexicoking. Both gasify the coked resid.

Combustion Sources

Major refineries contain furnaces in processes such as crude distillation that are as large as a furnace in a 100-MW power plant. Demonstration of a flue-gas cleaning system for such furnaces may be useful in defining possibilities for control of such systems and may adapt the furnaces for use of high-sulfur fuel. One of the by-product flue-gas cleaning processes may be especially appropriate since most refineries are already in the sulfur recovery business.

Discussion

The usefulness of any of the demonstrations will depend in part on EPA's planned approach to refinery control. It is doubtful that any of the processes identified present serious technical problems that most refiners could not solve for themselves. Hence the situation is not analogous to that in the utilities industry where help is needed in the solution of the technical problems. Justification for undertaking demonstrations probably is related to economic clarification or to support base standards, rather than to solution of technical problems.

There is some evidence to suggest that some companies (especially the largest ones) in the industry will not readily welcome EPA cooperation in what is considered the industry's area of responsibility. However, probably not all refiners share this sentiment. One consultant suggested that the moderate-sized refiners would welcome assistance and suggested contact with Petrofina, Ashland and Pasco. The smaller refiners would not have the economic or technical capability or physical facilities necessary to cooperate in a demonstration program.

V. CONCLUSIONS AND RECOMMENDATIONS

Methodology

The principal conclusions relating to methodology are as follows:

(1) The methods developed for use in generating industry profiles and identification of the processes which comprise the industry appear, on the basis of their application to two dissimilar industries, to be generally applicable for systematic study of any industry.

(2) Expert opinion can be used to develop the perspective needed to understand environmental effects of a given industry if a proper approach is used. Consideration should be given to selection of experts who are affiliated directly with the industry and others who are knowledgable but not employed directly by companies in the industry. This appears to help insure that problems are kept in proper perspective.

(3) Also, it appears that at least three experts should be consulted. Where fewer are used there seems to be a good chance that experience gaps can lead to development of an inaccurate concept of some controversial issues.

(4) Also, it would appear that at least one paid consultant be used where review of industry profiles are concerned. Few of the experts employed by industry who cooperated without compensation found time for a detailed review of the draft version of the industry profiles that had been supplied for criticism.

(5) Finally, it was evident that careful preparation prior to contact with experts was necessary to assure that maximum benefit was obtained. Preparation of the best possible industry profile and complete list of potential

new processes would help to bring in outside help and inputs.

(6) If future studies are undertaken, a document describing EPA's policies and procedures for demonstration studies should be made available to industry representatives who are to be contacted. Such a document would have been helpful in eliminating the suspicions and reservations relating to loss of proprietary rights and trade secrets, etc.

Demonstration Opportunities in Secondary Non-Ferrous Smelting Industry

The principal conclusions relating to demonstration opportunities in the secondary non-ferrous smelting industry are as follows:

(1) The secondary non-ferrous metals industry is in need of assistance in reducing or eliminating atmospheric emissions from the numerous processes involved throughout the entire industry. However, the majority of the companies that make up the secondary non-ferrous metal industry are medium-sized privately-owned companies and are not generally equipped to deal with the development and application of new technology for control of pollution. They lack the technical capability and financial resources which are needed.

(2) There is an indication that some work toward pollution abatement in the secondary nonferrous metals industry is underway and its application might be accelerated if demonstrations were given partial support. Such support might also encourage the industry to undertake additional work. From this standpoint, projects in this industry should enjoy high priority.

(3) The Environmental Protection Agency has developed an image in some instances as being a "police" force. Consequently, companies are reluctant to enter into agreements with the

Federal Government which would give the representatives of EPA access to company data. However, some companies would welcome assistance in this area.

(4) Industry is concerned that any venture with the Federal Government may result in loss of patent rights to the process. The secondary nonferrous industry is very competitive and each company guards its secrets very closely. If companies can be assured that rights will be guarded, they may be willing to enter into jointly-funded ventures.

(5) Although companies in the industry produce different products, many of the pollutants are similar and in many cases, the same. Thus, pollution problems are common to several segments of this industry. For example, sulfur oxide emission is a common pollutant to the copper and lead segments of both the secondary and primary nonferrous metals industries while the manufacturing operations are different. It was the opinion of officials from several companies that emphasis in pollution abatement should be directed wherever possible toward the development of add-on pollution control equipment rather than process modification. Such equipment could then be used by several segments of industry and, thus, many could benefit rather than a few. Also development of add-on equipment could be conducted without disclosure of company secrets.

Demonstration Opportunities in the Petroleum Refining Industry

The principal conclusions relative to demonstration opportunities in the petroleum refining industry are as follows:

(1) In general the industry understands its problems and has available to them the technology needed to solve their own problems. Further they are financially in a better position to support the work necessary to bring their problems under control than many other industries.

(2) The companies refining petroleum vary widely in size. The large companies neither need or would welcome government support for projects. The small companies ~~would~~ generally lack financial capability and technical support to participate in such studies. The medium size companies would appear to be the most likely to have the capability and motivation to participate in jointly funded work.

APPENDIX A

NOMENCLATURE

LIST OF EXPERTS FOR PETROLEUM REFINING INDUSTRY

LIST OF EXPERTS FOR SECONDARY NONFERROUS METALS INDUSTRY

NOMENCLATURE

1. RAW MATERIALS are feed materials for processes. They are of two types: primary raw materials that are used in the chemical form that they were taken from the land, water or air and secondary raw materials that are industrial intermediate products.
2. INDUSTRIES are made up of groups of companies that are considered competitors in production of the same products. Industries have an identifiable population of companies and have a high degree of commonality with respect to raw materials consumed, processes employed, products produced, environmental control problems experienced, pollutants produced and control equipment used.
3. OPERATIONS are general industrial procedures by which materials are processed or products produced. Operations can consist of a series of processes, or can be accomplished by two or more alternative processes.
4. PROCESSES are the basic units that collectively describe industries. Processes comprise specific arrangements of equipment that accomplish, in a distinct way, chemical or physical transformation of input materials into end products, intermediate products, secondary raw materials or waste materials. Other process outputs include waste streams to the air, water, or land. Input materials can include primary or secondary raw materials, waste materials, or intermediate products. Where two or more different combinations of process steps accomplish the same chemical or physical transformation but have different environmental impacts (e.g., different emission characteristics), each combination is a distinct process.

5. PROCESS STEPS are the basic components of a process that utilize process equipment or materials handling equipment (process equipment does not include control equipment). In cases where a piece of process equipment has two or more cycles or phases of operation with distinctly different emissions to the atmosphere, such cycles or phases can be considered sequential process steps.
6. SOURCES are process steps from which significant amounts of air, water, or land pollution can be discharged.
7. CONTROL EQUIPMENT is equipment whose primary function is to reduce emissions to the atmosphere. Its presence is not essential to the economic viability of the process.
8. COMPANIES include corporate sub-divisions that have a product slate similar to other companies in an industry.
9. PLANTS are comprised of collections of processes to produce the products associated with their industry. Individual plants within an industry may employ different combinations of processes but all plants will have some of the processes that are common to the industry.
10. END PRODUCTS include only those process outputs that are marketed for use or consumption in the form that they exit from the process. After use, an end product becomes a waste material.
11. INTERMEDIATE PRODUCTS are process output streams that go either to other processes in the same industry in which they are produced, or to other industries where they become secondary raw materials.
12. WASTE MATERIALS are either process outputs that go to a scavenging industry, or are used end products that are disposed or processed to recover reusable constituents.

LIST OF EXPERTS FOR PETROLEUM REFINING INDUSTRY

Mr. W. L. Lewis
Mr. H. H. Meredith
The Exxon Company
P. O. Box 2180
Houston, Texas

Mr. E. Lewis Whittington
Mr. A. G. Sliger
Dr. W. F. Hoot
M. W. Kellogg Company
1300 Three Greenway Plaza East
Houston, Texas 77046

Mr. Lee H. Solomon
Turner, Mason, and Solomon
1950 Mercantile Dallas Building
Dallas, Texas 75201

Mr. David Moore
Battelle-Columbus Laboratories
505 King Avenue
Columbus, Ohio 43201

Mr. Paul W. Spaite
Consulting Engineer
6315 Grand Vista Avenue
Cincinnati, Ohio 45213
Telephone (513) 731-3991

LIST OF EXPERTS FOR SECONDARY NONFERROUS METALS INDUSTRY

	Name and Address	Area of Expertise
1.	Albert L. Belcher, Bob Merritt National Lead Company Hightstown, New Jersey	Lead
2.	John A. Bitler Manager, Manufacturing General Battery Corp. Reading, Pennsylvania	
3.	Dr. H. B. Bomberger Director, Metallurgy Research Center RMI Company Niles, Ohio Telephone (216) 652-9951	Titanium
4.	J. P. Brull, President, Barth Smelting & Refining Co. Newark, New Jersey	Titanium
5.	H. S. Caldwell, Jr. U.S. Bureau of Mines College Park, Maryland Telephone (301) 344-4027	General
6.	V. A. Cammarota Mercury Specialist Division of Nonferrous Metals U.S. Bureau of Mines 4015 Wilson Blvd. Arlington, Virginia 22303	Mercury
7.	Cobalt Information Center Battelle Memorial Institute Columbus, Ohio 43201	Cobalt
8.	Mr. Denton Dept. of Commerce Washington, D. C.	
9.	Ray Familar Manager of Engineering Cook County Air Pollution Dept. Chicago, Illinois	Cadmium

	Name and Address	Area of Expertise
10.	Dr. R. Foos Brush Beryllium Company Cleveland, Ohio	Beryllium
11.	E. Godsey American Smelting and Refining Company Salt Lake City, Utah	Aluminum
12.	Bruce G. Gonser Consultant Battelle Memorial Institute Columbus, Ohio 43201	General
13.	Keith Harris Division of Nonferrous Metals U.S. Bureau of Mines 4015 Wilson Blvd. Arlington, Virginia 22303	Tin
14.	Crawford Hayes Chief Project Engineer Bridgeport Brass Company Bridgeport, Connecticut 06602 Telephone 366-6182	Brass and Bronze
15.	Robert Henning, President Belmont Smelting Company 330 Belmont Avenue Brooklyn, New York 11207	Cadmium
16.	Dr. Kapplain U.S. Bureau of Mines Washington, D. C.	General
17.	B. Langston U.S. Reduction Company East Chicago, Illinois	Aluminum
18.	Dr. Thomas Leontis Magnesium Research Center Battelle Memorial Institute Columbus, Ohio 43201	Magnesium
19.	Dr. K. Libsch National Lead Company Hightstown, New Jersey	Lead
20.	Earl R. Marble, Jr. Consulting Engineer P.O. Box 816, Brainy Boro Station Metuchen, New Jersey 08840 Telephone (201) 548-4990	Aluminum, Brass & Bronze, Copper Lead, Tin, Zinc

	Name and Address	Area of Expertise
21.	Drew Meyer Vulcan Material Company Box 720 Sandusky, Ohio 44870 Telephone (419) 626-4610	Tin
22.	R. L. John Minnick Vice President, R&D Plymouth Meeting, Pennsylvania	
23.	Stanton Moss Manager, George Sall Metal Company 2255 East Butler Street Philadelphia, Pennsylvania 19137 Telephone (215) 743-3900	Aluminum, Brass, Bronze
24.	Howard Ness National Association of Secondary Metal Industries New York, New York Telephone (212) 867-5000	
25.	H. R. Ogden Magnesium Research Center Battelle Memorial Institute Columbus, Ohio 43201	Magnesium
26.	Dr. W. R. Opie, Vice President M. Houser, Plant Manager Amax Company Carteret, New Jersey	General
27.	Allan Payne United Refining and Smelting Company 3700 N. Runge Avenue Franklin Park, Illinois Telephone (312) 455-8800	Precious Metals
28.	Milo Peterson Chairman of Committee, SIC Office of Management and Budget Washington, D. C.	
29.	Dr. Carl Rampacek U.S. Bureau of Mines Washington, D. C.	General
30.	R. W. Roe (and J. Henderson, Sup't of Research) Director of Research ASARCO South Plainfield, New Jersey	General

	Name and Address	Area of Expertise
31.	William Shirley Apex Smelting Company Des Plaines, Illinois	Aluminum
32.	Paul W. Spaite Consulting Engineer 6315 Grand Vista Avenue Cincinnati, Ohio Telephone (513) 731-3991	General
33.	Albert W. Spitz & Associates Consultants Wyncote, Pennsylvania Telephone (215) 884-7182	Lead, Tin, Precious Metals, Cadmium
34.	S. F. Tauben Diversified Metals Hazelwood, Missouri	
35.	Tin Research Institute 483 West 6th Street Columbus, Ohio 43201 Telephone (614) 294-3341	Tin
36.	R. R. Wells Director, Abany Metallurgy Research Center Abany, Oregon Telephone (503) 926-5811, Extension 220	Nickel
37.	Battelle-Columbus Personnel Marty Forkas H. Barr R. Bengston Columbus, Ohio 43201	

APPENDIX B

THE PETROLEUM REFINING INDUSTRIAL PROCESS PROFILE

INDUSTRY DESCRIPTION

The petroleum refining industry processes crude oil into a large number of products including liquefied petroleum gas, gasoline, kerosine, aviation fuel, diesel fuel, a variety of fuel oils, and lubricating oils. Some of the processes involved in the manufacture of these products are: distillation, absorption, extraction, thermal and catalytic cracking, isomerization, hydrogenation, dehydrogenation, polymerization, etc.

Each refinery is more or less unique in that each operation is carried out using equipment designed to meet needs peculiar to a particular location. It is possible, however, for purposes of analysis to consider all refineries as consisting of some combination of the 29 process modules shown in Table B-1. Figure B-1 is a flow diagram showing the interrelationships between these processes.

Only a few refineries employ all the processes shown in Figure B-1 because some of the processes are (1) proprietary, (2) representative of a limited size range of refineries, (3) typical of a limited time period, and (4) designed for a particular crude oil. In addition to the processes shown, several hundred other process variations are used at a few refineries. Most of these processes are minor variations of the processes shown in Figure B-1. Larger refineries generally use most of the processes shown. American refineries typically use more processes than foreign refineries because they are designed to produce a maximum amount of motor fuel. European refineries are designed to produce a higher percentage of heating fuels. The complex American refineries produce a minimum of residual oil. Less complex Caribbean refineries with minimum cracking facilities to supply local needs for motor fuels are major suppliers of fuel oil for the U. S. East Coast.

TABLE B-1. LIST OF PETROLEUM REFINERY PROCESSES(1)

	Process	Process Type	US Capacity(2) MM bbl/SD Jan., 1972	Feed	Products	Effluents	Energy Required		
							Electrical-Mechanical, kwhr/bbl	Steam, lb/bbl	Fired-Heaters, MBtu/bbl
(1)	Crude Storage	Open	A	Crude	Crude	Water	b	b	b
(2)	Desalting	Closed	a	Crude	Dry Crude	Salt Water	0.01	22	0
(3)	Crude Distillation	Closed	13.7	Crude	Refinery Gas Natural Gasoline Kerosene Distillate Fuel Oil Gas Oil Topped Crude	Water	0.1-0.6	15	100
(4)	Vacuum Distillation	Closed	4.9	Topped Crude	Gas Oils Vacuum Residual	Water Vent gas	0.1-0.3	8	50
(5)	Chemical Sweetening	Closed	b	Sour Distillate	Sweet Distillate	Spent Chemicals	0.01	b	b
(6)	Hydrogen Generation	Closed	b	Hydrocarbon	Hydrogen	Carbon Dioxide	b	b	0-300
(7)	Naphtha Hydrogen Treating	Closed	2.8	Gasoline	Gum-Free and Sulfur-Free Gasoline	Spent Catalyst	1.4	30-90	0-50
(8)	Kerosene Hydrogen Treating	Closed	1.0	Sour Kerosene	Desulfurized Kerosene H_2S	Spent Catalyst	0.5-2	8	0-70
(9)	Gas Oil Hydrogen Treating	Closed	4.9[c]	Gas Oil	Desulfurized Gas Oil H_2S	Spent Catalyst	2	1-10	5-70
(10)	Lubricating Oil Hydrogen Treating	Closed	4.9[c]	Sour Lube Oil	Desulfurized Lube Oil H_2S	Spent Catalyst	2.5-9	15-28	35-140
(11)	Residual Oil Hydrogen Treating	Closed	0	High-Sulfur Residual	Low-Sulfur Residual H_2S	Spent Catalyst	1-4	3-25	60-100
(12)	Catalytic Hydrocracking	Closed	0.84	Gas Oil Residuals	Refinery Gas Gasoline Diesel Oil Furnace Oil	Spent Catalyst Gas from Regeneration	1-6	(6)-18	100-250
(13)	Gas Processing	Closed	1.3	Mixed Gases	Fuel Gas PG Butanes Light Gasoline Olefines	-	2	0	0
(14)	Amine Stripping	Closed	a	Hydrocarbon H_2S-Stream	Sulfur-Free Hydrocarbons	Waste Amine	0.5	(1)[d]	0
(15)	Sulfur Manufacture	Open	1.2[e]	H_2S	Sulfur	Tail-Gas	0.1	(4)[d]	0.4[f]

(1) See list of references at end of report.

TABLE B-1 (Continued)

	Process	Process Type	US Capacity MM bbl/SD Jan., 1972	Feed	Products	Effluents	Energy Required		
							Electrical-Mechanical kwhr/bbl	Steam, lb/bbl	Fired Heaters, MBtu/bbl
(16)	Isomerization	Closed	0.2	N-Butane	Isobutane	Spent Catalyst	1.2	20	30
(17)	Catalytic Reforming	Closed	3.2	Naphtha	Aromatics Hydrogen LPG Isobutane	Spent Catalyst Gas from Regeneration	3-6	0	200-400
(18)	Fluid-Bed Catalytic Cracking	Open	4.0	Gas Oil	Refinery Gas Gasoline Heating Oil	Flue Gas Water Spent Catalyst	0.4-3	(70)-40	0-70
(19)	Moving-Bed Catalytic Cracking	Open Open	0.59	Gas Oil	Refinery Gas Gasoline Heating Oil	Flue Gas Water Spent Catalyst	0.1-1.5	(60)-100	100-300
(20)	Visbreaking	Closed	0.23	Topped Crude, Vacuum Residual	Refinery Gas Fuel Oil Gas Oil		1.8	(80)	260
(21)	Coking	Closed Open	g	Residual	Refinery Gas Gasoline Fuel Oil Coke	Wash Water Flue Gas	15	(100)	350
(22)	Polymerization	Closed	0.12	Olefins	Gasoline	Spent Catalysts	1.2	20	0
(23)	Alkylation	Closed	0.8	Isobutane Olefins	Gasoline LPG	Spent Acid	5-10	100-300	0
(24)	Lube Oil Processing	Closed	0.22	Vacuum Gas Oil Vacuum Residual	Lube Oil Wax		2-10	100-400	0
(25)	Asphalt Processing	Closed Open	0.62	Vacuum Residual	Asphalt	Gas from Air-Blowing	0.1-3 1	50-300 0	100-300 5-10
(26)	Storage and Blending	Closed	a	Process Streams	Products	Breathing and Vent Gases	b	b	0
(27)	Prime Movers Electric Steam IC	 Closed Closed Open	 a a a	 - Steam Fuel	Power Power Power	None None Flue Gas Used Oil	N.A. N.A. N.A.	0 N.A. 0	0 N.A. 0
(28)	Steam Generation	Open	-	Any Fuel	Steam	Flue Gas Ash Water-Treatment Sludges	b	-	-
(29)	Process Heaters	Open	-	Gas-Liquid Fuels	Heat	Flue Gas	b	-	-

a - Not available, large
b - Not available, small
c - All hydrogen treating
d - lb steam/lb H_2S
e - Million tons/year
f - M Btu/lb sulfur
g - 41,000/tons/sd of coke
( ) - Production rather than use
N.A. - Not applicable

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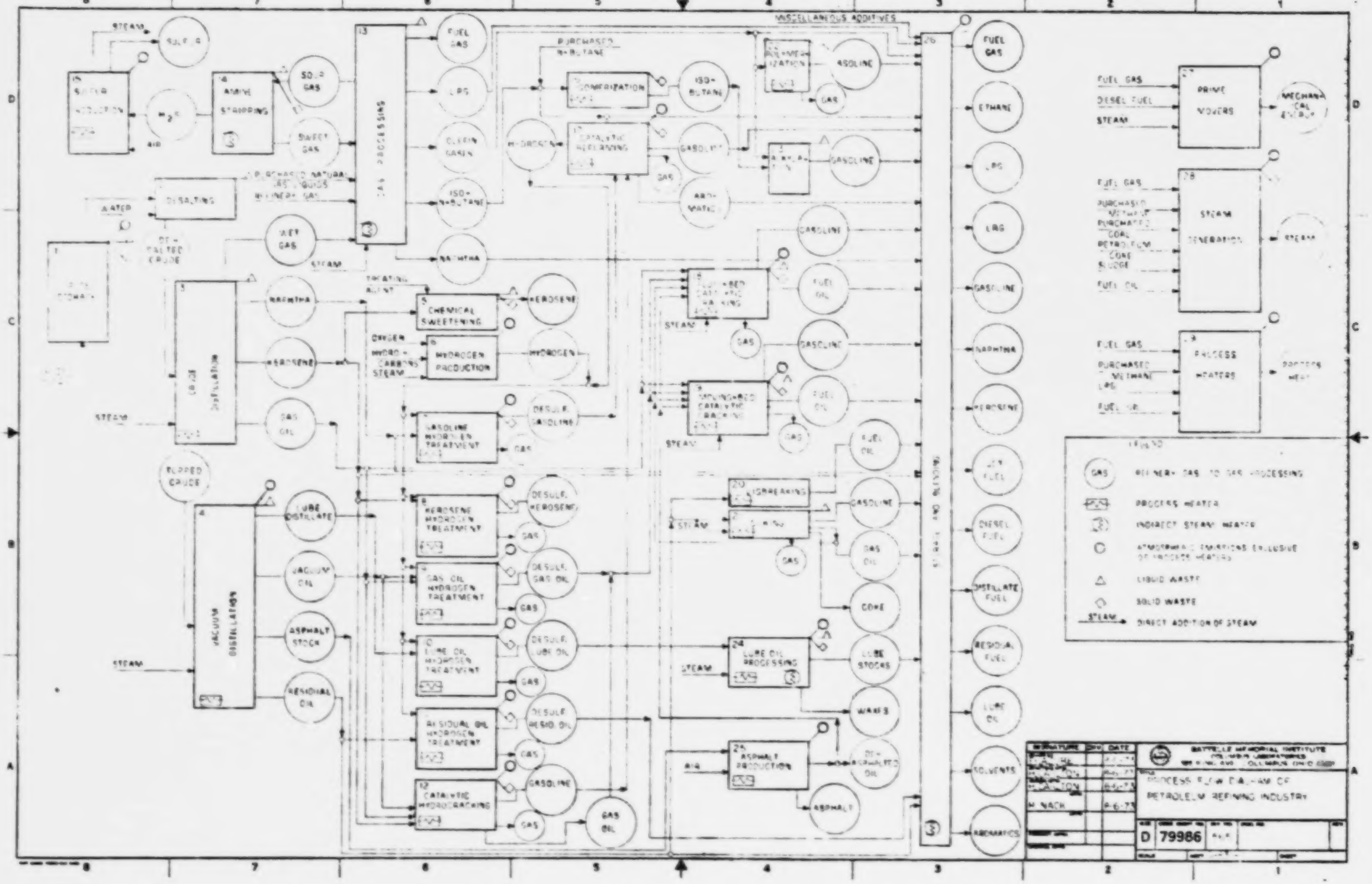

STEAM
SULFUR
15 SULFUR REDUCTION
H_2S
AIR
14 AMINE STRIPPING
SOUR GAS
SWEET GAS
13 GAS PROCESSING
FUEL GAS
LPG
OLEFIN GASES
ISO-N-BUTANE
NAPHTHA
PURCHASED NATURAL GAS LIQUIDS
REFINERY GAS
WATER
DESALTING
DE-SALTED CRUDE
WET GAS
STEAM
1 CRUDE STORAGE
3 CRUDE DISTILLATION
NAPHTHA
KEROSENE
GAS OIL
STEAM
TOPPED CRUDE
4 VACUUM DISTILLATION
LUBE DISTILLATE
VACUUM OIL
ASPHALT STOCK
RESIDUAL OIL
TREATING AGENT
5 CHEMICAL SWEETENING
KEROSENE
OXYGEN
HYDRO-CARBONS
STEAM
6 HYDROGEN PRODUCTION
HYDROGEN
7 GASOLINE HYDROGEN TREATMENT
DESULF. GASOLINE
8 KEROSENE HYDROGEN TREATMENT
DESULF. KEROSENE
9 GAS OIL HYDROGEN TREATMENT
DESULF. GAS OIL
10 LUBE OIL HYDROGEN TREATMENT
DESULF. LUBE OIL
11 RESIDUAL OIL HYDROGEN TREATMENT
DESULF. RESID. OIL
12 CATALYTIC HYDROCRACKING
GASOLINE
GAS OIL
GAS
PURCHASED N-BUTANE
ISOMERIZATION
ISO-BUTANE
HYDROGEN
17 CATALYTIC REFORMING
GASOLINE
AROMATICS
POLYMERIZATION
ALKYLATION
GASOLINE
MISCELLANEOUS ADDITIVES
FLUID-BED CATALYTIC CRACKING
FUEL OIL
MOVING-BED CATALYTIC CRACKING
FUEL OIL
20 VISBREAKING
COKING
FUEL OIL
GASOLINE
GAS OIL
COKE
24 LUBE OIL PROCESSING
LUBE STOCKS
WAXES
25 ASPHALT PRODUCTION
DE-ASPHALTED OIL
ASPHALT
AIR
26 PRODUCT BLENDING
FUEL GAS
ETHANE
LPG
LRG
GASOLINE
NAPHTHA
KEROSENE
JET FUEL
DIESEL FUEL
DISTILLATE FUEL
RESIDUAL FUEL
LUBE OIL
SOLVENTS
AROMATICS
FUEL GAS
DIESEL FUEL
STEAM
27 PRIME MOVERS
MECHANICAL ENERGY
FUEL GAS
PURCHASED METHANE
PURCHASED COAL
PETROLEUM COKE
SLUDGE
FUEL OIL
28 STEAM GENERATION
STEAM
FUEL GAS
PURCHASED METHANE
LPG
FUEL OIL
29 PROCESS HEATERS
PROCESS HEAT
LEGEND
GAS REFINERY GAS TO GAS PROCESSING
PROCESS HEATER
INDIRECT STEAM HEATER
ATMOSPHERIC EMISSIONS EXCLUSIVE OF PROCESS HEATERS
LIQUID WASTE
SOLID WASTE
STEAM DIRECT ADDITION OF STEAM
BATTELLE MEMORIAL INSTITUTE
COLUMBUS LABORATORIES
COLUMBUS, OHIO
PROCESS FLOW DIAGRAM OF PETROLEUM REFINING INDUSTRY
M NACK
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FIGURE B-1. PROCESS FLOW DIAGRAM OF PETROLEUM REFINING INDUSTRY

Companies

As of January 1, 1973, 121 companies operated 245 refineries in the United States. Table B-2 lists the 16 largest refiners and the processing capacity of these companies along with the combined capability of the other 105 refiners.(9)

The table indicates that refineries of the largest companies average about 100,000 bbl/day capacity* while the refineries of the smaller companies average about 20,000 bbl/day. In addition, the smaller refineries are less complex than the larger refineries.

Size

The largest refinery processes about 400,000 barrels of crude oil per day and covers 1,100 acres. Refineries with capacities greater than 100,000 bbl/day process about 56 percent of the total crude oil and more than 80 percent of the total is processed in refineries exceeding 50,000 bbl/day. On the other hand, operating refineries process as little as 1,000 bbl/day; however, only special circumstances--such as a remote location (two new small refineries were built on Alaska's north slope) or a specialty product, lubricating oil, asphalt, etc.--permit economic operation of small refineries.

Location

Refineries are located in 39 states. However, 50 percent of the total capacity is concentrated in Texas, California, and Louisiana, adjacent to both major oil fields and deep water ports. Other locations with many large refineries, and perhaps 25 percent of U. S. crude oil capacity, are

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* Capacity in the refinery industry is reported on a barrel per stream/day (BPSD) basis; i.e., the capacity of the unit when operating. Because of maintenance shutdowns, this capacity is about 5 percent greater than the long-term capacity of the crude still and 10 percent greater than the long-term capacity of other process units.

TABLE B-2. LIST OF REFINERS

	No. Refineries	Crude Capacity, bb/sd	Cat Cracking Feed bb/sd	Cat Reforming	Hydro-cracking bb/sd	Other Hydro Processing bb/sd	Alkylation bb/sd
(1) Exxon	5	1,211,100	487,900	273,600	70,900	614,268	81,500
(2) Texaco	12	1,160,000	443,300	232,600	38,900	329,300	56,200
(3) Shell	8	1,123,500	368,000	278,900	105,900	693,500	72,100
(4) Amoco	10	1,061,000	342,800	243,800	40,000	278,200	47,150
(5) Standard (Calif.)	13	1,019,000	208,000	246,000	173,400	234,200	38,700
(6) Mobil	9	969,300	335,200	241,900	47,000	407,600	63,000
(7) Gulf	8	869,800	319,000	227,800	40,400	409,400	70,000
(8) ARCO	6	803,600	210,000	247,000	86,500	390,000	28,700
(9) Sun	5	496,000	202,000	143,800	26,000	148,300	37,200
(10) Union	4	465,900	129,300	122,000	51,000	245,800	28,500
(11) Sohio/BP	5	428,300	144,900	114,500	55,000	170,800	22,900
(12) Phillips	6	422,200	173,800	111,600	22,000	140,200	43,100
(13) Conoco	7	342,500	103,100	79,200	--	121,900	18,000
(14) Ashland	7	273,500	119,000	58,000	--	164,000	14,000
(15) Cities	1	245,000	112,500	39,000	6,000	51,500	26,000
(16) Marathon	3	234,500	73,700	57,000	22,000	57,500	11,750
105 Smaller Companies	136	2,763,500	739,500	557,200	80,000	772,000	153,245
TOTAL	245	13,991,580	4,512,050	3,273,918	865,000	5,228,488	812,045

in New Jersey and Pennsylvania serving the East Coast population, and in Illinois, Indiana, and Ohio near major consuming regions.

Refineries frequently interchange products and raw materials with neighboring plants of other industries. Common neighbors are petrochemical plants (which use some of the refinery products and often generate as byproduct materials similar to some of the refinery intermediate products which then are sold to the refinery), and electric generation plants (which may buy fuel from the refinery and supply the refinery with steam and electric power).

Future Trends

The petroleum industry has been expanding at the rate of about 4 percent per year. With the recent (1972) modification of oil import regulations and current gasoline shortage, the rate of expansion can be expected to increase to 5 or 6 percent per year. However, because of lead times required, the increased rate of expansion is not expected for two or three years, i.e., until 1976.

Another major future trend in petroleum refining is the increasing dependence on imported crude oils. The imported crudes contain more sulfur than the American crudes. Therefore, increased quantities of sulfur will be entering the refineries and the sulfur will be removed from the oil in various processes to meet both product quality standards and pollution control standards. Some refineries cannot process high-sulfur crudes because of corrosion problems, although these problems can be expected to be solved by replacing mild steel components with corrosion resistent components during periodic maintenance shutdowns. Other processing changes can be expected. Most of the chemical sweetening processes (Process 5)* change the form of the sulfur in the petroleum rather than remove it. With the higher levels of sulfur, removal is required. Therefore, chemical sweetening processes are becoming obsolete, and are being replaced with sulfur removal processes (No. 7, 8, 9, 10, and 11). The sulfur removal processes require hydrogen, resulting in use of hydrogen generating processes (No. 6 and 17). Sulfur plants will also be installed to make sulfur from the hydrogen sulfide produced by the sulfur removal processes.

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* See Page 18.

The petroleum industry is already a major supplier of sulfur, supplying over 1,000,000 tons (10 percent) of about 10,000,000 tons used in this country. In 1970, only about 25 percent of the sulfur in the crude oil was recovered as elemental sulfur. With increasing desulfurization of products, and increasing sulfur in the crude, the industry could become the largest supplier of sulfur in the country.

Another trend is toward manufacture of nonleaded high-octane gasolines. Alkylation (Process 23)* and catalytic reforming (Process 17) capacities are being expanded to meet the demand for higher octane fuels. Catalytic reforming requires a sulfur-free feed. Naphtha desulfurization (Process 7) capacity is being expanded tc supply this fed. Because of the higher octane ratings needed, less straight-run gasoline from the still (Process 3) can be blended into the final product. Catalytic cracking (Processes 18 and 19), coking (Process 21), and polymerization (Process 22), also make high-octane components that are blended into lead-free gasoline.

ENVIRONMENTAL IMPACTS

Atmospheric Emissions

The air contaminants emitted from process equipment include hydrocarbons, carbon monoxide, particulates, sulfur and nitrogen compounds, and odoriferous materials such as mercaptans. The various processes listed in Table B-1 are classified as open or closed. Open systems vent gases to the atmosphere in normal operation. The vented gases may be contaminated and cause pollution. The major open process from an air emission standpoint is the catalytic cracker regenerator which vents gas from burning of coke deposits on the catalyst.

Closed systems do not vent process gas to the atmosphere and emissions would be only from leaks or possibly from the vents of steam ejector vacuum pumps. Storage tanks are a special case where air in the tank is contaminated with hydrocarbons and may vent to the atmosphere.

Since the energy required for a 400,000 bbl/day refinery is about the same as the energy required for a 1,000 megawatt steam electric generating station, the potential air pollution from combustion sources in the refinery is very great. Although particulates and sulfur oxides may be emitted in somewhat reduced amounts.

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* See under "PROCESSES" starting on Page B-14.

Liquid Effluents

Liquid effluents are: condensed steam from various processes, cooling water from many processes, tank-cleaning wastes, spent chemicals, and some spilled oil. All refineries have an oil-water separator on the sewage system to stop oil from being discharged into nearby streams. Process water is frequently sour (hydrogen sulfide--H_2S) so it is stripped of its acid (H_2S) before discharge.

Solid Wastes

The major solid waste from refineries is spent catalyst which usually is landfilled. Sludges from the cleaning of equipment storage tank, oil-water separator, etc., and from lube oil manufacture also cause a solid waste problem. The sludges may be burned or otherwise disposed of.

RAW MATERIALS

The major raw material processed in a refinery is crude oil (11,210,000 bbl/day).(3) A group of materials called natural-gas liquids (1,699,000 bbl/day) is the other major raw material. Various secondary raw materials are transferred between refineries and imported. Many materials are purchased and blended into the products in small quantities; for example, alkyl lead into gasoline and barium salts into diesel fuel.

Crude oil composition varies widely depending upon its sources. Petroleum is a mixture of paraffinic, naphthenic, and aromatic hydrocarbons containing small amounts of sulfur, oxygen, and nitrogen compounds, plus trace quantities of various metals such as vanadium and nickel.

Many different chemical compounds (probably over 3,000)(4) are present in crude petroleum and additional compounds are made during refining processes. The hydrocarbons are generally grouped into series such as the paraffins, the olefins, the naphthenes, the aromatics, and polycyclic compounds.

The sulfur in the crude is a major source of sulfur dioxide pollution as most of the refinery products ultimately are burned. If the sulfur is not removed in the refining process, it will be emitted as a pollutant when the products are used. Sulfur may be present as free sulfur, hydrogen sulfide, or in organic compounds such as thiophenes, mercaptans, and alkyl sulfides. The mercaptans are particularly obnoxious from an odor standpoint and are sometimes oxidized to disulfides to reduce the odor, if sulfur removal per se is not required.

Natural-gas liquids, which are also called natural gasoline or casinghead gasoline, are hydrocarbons other than methane in natural gas as it comes from gas wells. They are separated from the methane by the natural gas industry and sold to refineries. Natural gas liquids are similar in composition to various light naphtha streams in the refinery and are blended and/or processed with them.

Various materials are purchased for their fuel value at the refinery; natural gas is most common and frequently is used in process heaters. The steam boiler usually can be adapted to burn any fuel, so the fuel used here is determined by supply and cost.

Other miscellaneous materials are purchased. The n-butane (feed to the isomerization process or used for gasoline blendings) is both purchased from the natural gas industry and supplied by other refinery processes. Many additives for blending into the various products are purchased; these include alkyl lead for motor gasoline, barium compounds for diesel fuels, and additives for lubricating oils such as detergents viscosity index improvers, and antioxidants.

PRODUCTS

Approximately 2,500 products are currently produced wholly or in part from petroleum. A record 15,160,000 bbl/day of petroleum products were consumed in the United States in 1971.(2) Table B-3 lists the major petroleum products and their consumption (1971). Most petroleum products are blends of several refinery streams and the same material often has a

TABLE B-3. MAJOR PETROLEUM PRODUCTS, 1971

Product	Consumption bbl/day	Net Import
Gasoline	5,992,000	51,000
Jet fuel	996,000	161,000
Kerosene	250,000	0
Distillate fuel	2,691,000	149,000
Residual fuel	2,266,000	1,497,000
LPG and LRG	1,243,000	25,000[a]
Miscellaneous	1,722,000	133,000
Total	15,160,000	1,962,000

(a) Net export.

LPG - Liquefied Petroleum Gas

LRG - Liquefied Refinery Gas

different name when used for a different application. In addition, individual product specifications may be met by blends having different compositions when produced at different times or by different refineries.

Gasoline is almost one-half of the refinery output.(5) Its value is more than one-half of the value of all products sold by the refinery. The gasoline product is invariably a blend of naphthas from several refinery processes and includes several minor additives such as alkyl lead purchased from other industries. High octane rating, necessary for high compression engine fuel, is obtained from aromatic hydrocarbons which have octane ratings of about 100, naphthenic compound with side chains, and paraffinic hydrocarbons with several side chains. Butane and isopentane have good octaine ratings, but the amount of these compounds in gasoline is limited by their high volatility. Small additions of alkyl lead compounds substantially increase the octane rating of most gasolines.

Naphtha refers to hydrocarbon fractions boiling in the 90-400 F temperature range. Gasoline is a naphtha produced for use as motor fuel and designates both naphthas for blending into motor fuels and the final product. A single naphtha may be used both as a motor fuel and for other purposes such as a solvent and on feed to petrochemical industry.

Kerosene is a petroleum fraction boiling in the 350-550 F range. Historically, it was one of the first petroleum products and was used for lamps. For this use, kerosene usually is composed of paraffinic hydrocarbons which cause less smoking when burned in lamps. Various processes were developed to remove mercaptans from kerosene to reduce odor problems. Kerosene is used in small scale applications today such as domestic cooking.

Jet aircraft fuels are of two types, a kerosene type boiling in the 400-550 F range and a naphtha type boiling in the 250-550 F range. These fuels may be treated to reduce freezing point by removing wax and to reduce smoking by removing aromatic hydrocarbons.

Light diesel oil distills in 350-575 F range and can have a wide range of specifications; its performance is measured by a cetane rating that measures the ignition characteristics of the oil in a diesel motor. Fuels which naturally have a good cetane rating are used for diesel fuel while those with a poor rating are made into burner fuel.

Distillate fuels have similar boiling ranges to diesel oil. Any oils that can be distilled either in the crude still or in the vacuum still and oils of similar boiling ranges from various refinery processes are used as fuel oil. Generally, the oil is treated to remove sulfur. Distillate fuel is widely used for domestic heating.

Residual fuels are hydrocarbons left in the still after the volatile hydrocarbons have been distilled off. Most residual oils from the crude or vacuum still are diluted with kerosene or distillate oil, or visbroken to reduce viscosity or sulfur content. While residual oils are not treated to remove sulfur now, processes are being installed in refineries to remove sulfur from these oils. Residual oils are usually burned in large boilers used for electric power generation and steam generation in large industrial plants.

Asphalt is a hydrocarbon residue from asphaltic base crude oils. It is used with a rock (aggregate) as a cement in road pavement, for manufacture of roofing materials, and for many other applications. Petroleum coke is a residual from the coking process. It is used in the manufacture of electrodes for electric furnaces and also as a fuel.

Liquefied petroleum gas (LPG) is a mixture of C_2, C_3, and C_4 hydrocarbons. It is widely used for industrial heating and for domestic heating and cooking where natural gas is not available or scarce. Natural gas companies frequently add LPG to natural gas at times of peak demand. LPG is an excellent motor fuel with a high octane rating and minimum air pollutant emissions. It is occasionally used for truck or bus fleets and is quite widely used for fork lifts, payloaders, and other applications inside buildings because of low emissions from motors using LPG. Sometimes the designation LPG is restricted to a product of the natural gas industry and when that restriction is made, the same material made by the petroleum industry will be called liquefied refinery gas (LRG).

The petrochemical industry is based on olefins, LPG's, and aromatic hydrocarbons, which are secondary raw materials supplied in part by the natural gas industry. In addition, naphtha is cracked in a thermal cracking process to make ethylene. The cracking process is performed in both refineries and petrochemical plants. The refineries have long supplied aromatic hydrocarbons to the petrochemical industry. About 3 percent(5) of refinery output is used to petrochemical feedstock.

PROCESSES

Twenty-nine pertinent processes used in petroleum refineries are shown in Figure B-1 along with the flows of intermediate products among processes. Other refinery processes are not shown because (1) the process is a minor variation of a process shown, and the raw materials, products, and wastes are not significantly different from those in that process; (2) the process is a specific application, perhaps obsolete, and is not typical of the industry; or (3) the process, while performed in some refineries, is more typical of a different industry. Two variations of catalytic cracking are shown because their wastes are different. Each variation has several additional modifications, but they are not shown because the raw materials, products, and wastes are the same. A third variation, fixed-bed catalytic cracking, is not shown because the process is no longer widely used. Other processes, such as cracking naphtha to make ethylene, are considered part of the petrochemical industry and are not described, even though the processes are sometimes performed in a refinery.

Process heaters and process drives are treated as if they were processes because their emission is characteristic of the heater or drive and not of the particular process. Thus, the emissions and wastes shown for each process do not include those from heaters or drives. Emission from the heaters and drives are proportional to the energy requirements for the process.

A brief description of each of the 29 processes follows including information on processing techniques, equipment, raw materials, products, energy requirements, and wastes.

Crude Storage (1). Crude oil delivered to a refinery is stored in tanks until processed. The storage tanks are sized to receive the largest single shipment expected and to assure continuous operation of the refinery. The amount stored may be anywhere between a 2-week and a 2-month supply. The crude is stored in large cone or floating roof tanks of up to

250,000-barrel capacity. After storage, the oil is sent to the desalter if required and then to crude distillation.

Only a small amount of electrical energy is required for pumping of the stored crude.

Gaseous hydrocarbon emissions from storage tanks relate to three basic mechanisms: breathing loss, working loss, and standing storage loss. These are discussed later under storage and blending (Process No. 26). Less than 0.5 gal of water per bbl settles to the bottom of crude oil tanks and is sewered. This water effluent often contains salt. Some crude oils form sludges at the bottom of the storage tanks which are removed periodically and burned (usually in the steam boiler).

Desalting (2). The function of desalting is to remove salt, water, and water-soluble compounds from crude oil. Water is added to the oil and thoroughly mixed. The wet oil is heated to break the emulsion. The water is separated by decantation and sewered. In a variation of the process an electrostatic coalescer is used to separate the oil and water. The desalted crude is then fed to the crude still. Desalting is often performed in the oil field by the oil producing industry.

The thermal energy requirement for desalting is about 22,000 Btu/bbl assuming a 250 F desalting temperature and is usually obtained by heat exchange with one of the hot streams from the crude still. Alternatively, the oil may be heated with steam or a fired heater. About 0.01 kwh of mechanical energy per barrel is required to pump the oil through the system and to operate the electrostatic coalescer.

No gaseous emissions or solid wastes are produced from the process. About 2 gal of wastewater per barrel are drained from the desalter. This water contains any water-soluble material that had been in the crude and frequently is high in salt content. The wastewater volume is not very large--about 140 gpm from a 100,000-bbl/day refinery.

Crude Distillation (3). The function of crude distillation is to separate desalted crude oil into various products or intermediate products with different boiling points by distillation and steam stripping. The major items of equipment in crude distillation are the process heater (pipe heater), main distillation column, and stripping column. The number of product streams varies with the particular refinery.

The intermediate products are light naphtha, heavy naphtha, kerosene, distillate or diesel oil, gas oil, and topped crude. In a very simple refinery the intermediates are naphtha from the top of the still, gas oil from a side stream, and topped crude from the still bottom. In a complex refinery three to five side streams may be withdrawn.

In Figure B-1, the wet gas is shown as being processed further in the gas plant. However, in some refineries, this processing--the separation of light gases from their naphtha component--is performed as part of crude distillation. The naphtha is blended into motor fuels or any of several of the refinery products, or further processed to improve octane rating and/or reduce sulfur content. The kerosene may be chemically sweetened or hydrogen treated and sold directly or sent to blending. The distillate or diesel oil may be sold for diesel or fuel oil, hydrogen treated, hydrocracked, catalytically cracked, or blended. The gas oil may be sold as fuel oil, hydrogen treated, hydrocracked, catalytically cracked, or blended. The topped crude is usually the feed to the vacuum distillation process although it may be sold for fuel, blended into fuels, hydrogen treated, or catalytically cracked.

The installed capacity for crude distillation in the U. S. was 13.7 million barrels per stream day in 1971. The capacity of a crude still varies from about 1,000 to 200,000 barrels per day. The crude still is one of the largest items of equipment in the refinery.

Energy requirements include process heat from a heater, steam, and mechanical drives. About 100,000 Btu/bbl of crude are required from the process heater. The process heater associated with the crude still consumes 15 to 30 percent of the fuel used in a refinery and for the largest unit--200,000 barrels per day--the heat release in the heater is similar to the heat release in a boiler supplying a 100 MW electric generator. About 15 pounds of steam per barrel of crude are required to pump the raw materials and intermediate products.

No atmospheric emissions or solid wastes are produced under normal operating conditions. The steam used is condensed with the light naphtha in the condenser, separated from the oil by decanting, treated to remove acids and odors, and sewered. Operating conditions have little or no effect on wastewater. The amount of hydrogen sulfide in the wastewater is determined by the crude oil feed.

Vacuum Distillation (4). Vacuum distillation separates the atmospheric residue from the crude still into a heavy residual oil and one or more heavy gas oil streams. The major items of equipment are the process heater, the vacuum still, and the steam ejectors for producing the vacuum. The installed capacity for vacuum distillation is 4.9 million barrels per day (1971), which indicates that almost all of the topped crude is vacuum distilled.

Depending mainly upon the crude feedstock and partially upon the individual refinery, the residual oil intermediate product may be sent to the asphalt plant, thermally cracked in a coker to make gasoline, cracked in a visbreaker to make distillate fuel oils, blended into a fuel oil, or hydrogen treated to remove sulfur and then blended into a fuel oil. With suitable feedstocks the residual is sent to the lube oil process for manufacture into lubricating oil. The heavy distillate fraction from a paraffinic crude charge is sent to the lube oil plant either directly or through a hydrogen treating process. Other distillates are treated similarly to the gas oil stream from the crude still and catalytically hydrocracked, catalytically cracked, or used as fuel oil. The vacuum gas oil may be processed to remove sulfur by hydrogen treatment before catalytic cracking or use as a fuel oil. Refinery-to-refinery variations are minor.

About 50,000 Btu/bbl of thermal energy are required from a process heater. The product streams from vacuum distillation are usually cooled by heat exchange with the feed to the crude still to conserve energy. About 8 pounds of steam per barrel are required to operate the steam ejectors and to strip the residual and side streams of their lighter fractions. From 0.1 to 0.2 kwhr of mechanical energy per barrel are needed for pumping.

The vent gas from the steam ejectors contains about 130 lb of hydrocarbon vapors per 1,000 barrels of feed. The steam used in the injectors is condensed in a barometric condenser. The condensate may contain some oil. The wastewater eventually passes through an API oil-water separator, where the oil is removed before discharge of the water. No solid wastes are generated.

Chemical Sweetening (5). Chemical sweetening removes mercaptans from petroleum products to improve odor. At least 11 different processes are used for this purpose including contacting the petroleum material with various caustics, hypochlorites, solvents, or catalysts. In most processes, mercaptan sulfur is oxidized to an alkyl disulfide which is less obnoxious than the mercaptan. A few of the solvent processes separate the mercaptan which then becomes a product. The amount of petroleum products chemically sweetened is not known. A chemical sweetening process is installed in most of the older refineries while many newer refineries have replaced it with a final hydrogen treatment before blending.

The energy required by the process is minimal. Steam is used to strip mercaptans from solvents, but the solvent stream is much smaller than the petroleum stream. About 0.01 kwhr of mechanical energy per barrel is required for pumping.

Depending on the process, atmospheric emissions, liquid, and solid wastes are produced in small quantities. In some processes, the oxidizing chemical is regenerated by air blowing. In these processes air, slightly depleted in oxygen, is emitted. The amount of air used is proportional to the amount of mercaptan oxidizer. In hypochlorite processes, water containing sodium or calcium chloride is drained. The amount of salt is small and proportional to the amount of mercaptan sulfur oxidized. In one of the processes clay is used as a carrier for a copper chloride treating chemical and when the clay is inactivated it is sent to a landfill.

Hydrogen Plant (6). The hydrogen plant supplies hydrogen for hydrogenation reactions. Frequently, all hydrogen is supplied by catalytic reforming so that a hydrogen plant is not needed. Hydrogen is made by reacting naphtha or other hydrocarbons with steam at 1,400-1,600 F. The required temperature is obtained by external heating or by burning part of the hydrocarbon with oxygen rather than air to prevent dilution of the product hydrogen with nitrogen as illustrated in Figure B-2. The gas from the reactor contains hydrogen, steam, carbon monoxide, and carbon dioxide, and is passed through a shift reactor where CO and H_2O are catalytically reacted to form carbon dioxide and more hydrogen. The carbon dioxide is removed by adsorption. The small quantity of carbon monoxide remaining is catalytically oxidized

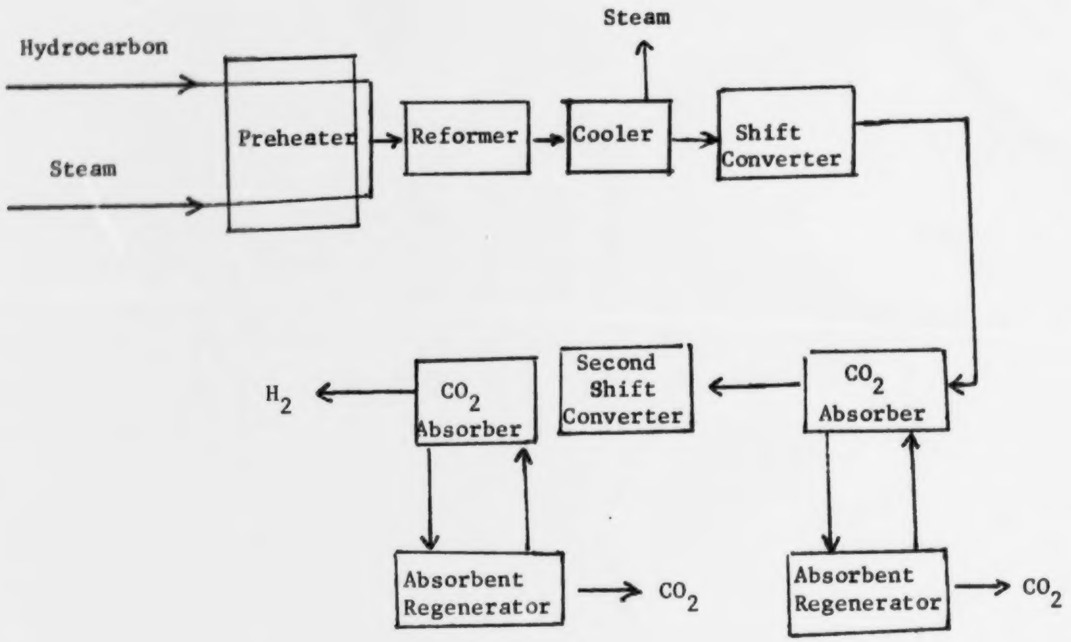
Steam
Hydrocarbon
Preheater
Reformer
Cooler
Shift Converter
Steam
H_2
CO_2 Absorber
Second Shift Converter
CO_2 Absorber
Absorbent Regenerator
CO_2
Absorbent Regenerator
CO_2

FIGURE B-2. HYDROGEN PLANT.

with steam to carbon dioxide and hydrogen and the last traces of carbon dioxide are absorbed with caustic or amine. The hydrogen is dried before use by condensation of water at high pressure. Single units as large as 10,000 scfm have been installed.

Thermal energy from steam is needed to strip the carbon dioxide from the absorber solution. Steam in about the same quantity is generated by cooling the gases from the partial oxidation of the feed in a boiler. With external heating about 300,000 Btu/bbl of feed are required. However, a substantial fraction can be recovered by heat exchange with the product. A small amount of mechanical energy is required for compression of the feed and pumping of the fluids through the systems if a liquid feedstock is used or about 4 kwhr/bbl are required if a gasoline feedstock is used.

The only waste stream from the process is a carbon dioxide atmospheric emission from regeneration of the absorber liquid. From 0.25 to 0.5 cubic foot of carbon dioxide is produced per cubic foot of hydrogen.

Naphtha Hydrogen Treatment (7). The function of the gasoline hydrogen treatment is to remove sulfur from a naphtha stream, saturate olefins to reduce gum formation, and/or remove aromatics from naphthas for solvents, burning fuels, or jet fuels. For gasoline treatment, the feed is mixed with about 400 cu ft of hydrogen per barrel, heated in a fired heater to 350-800 F and passed through a catalyst bed. The pressure is from 300 to 800 psi. The products are cooled, usually by heat exchange with the feed, and the excess hydrogen is separated and recycled. The gasoline product is reheated and steam stripped or distilled to remove hydrogen sulfide. A total of 4.9 million barrels per day (1971) of petroleum products are hydrogen treated, and 2.8 million barrels per day of catalytic reforming feedstock (naphtha(are hydrogen treated. The process product may be catalytically reformed or blended directly into a refinery product. The off-gas and hydrogen sulfide go to gas processing for further treatment.

Fired heaters require up to 50,000 Btu/bbl of gasoline treated. Since the reaction is exothermic, in some process variations all the necessary heat is supplied by the reaction. From 30 to 90 lb of steam per barrel are required to strip hydrogen sulfide from the gasoline. About 1.5 kwhr of mechanical energy per barrel are required to compress the hydrogen and to pump the feed through the system.

A gas stream containing carbon monoxide is emitted during infrequent (months to years) regeneration of the catalyst. The catalyst is regenerated by blowing a steam-air mixture through the bed to burn off a carbon deposit. A liquid stream of sour water is drained from the stripper in an amount equal to the steam used. The spent catalyst comprises a solid waste; however, catalyst life is usually more than 5 years. The catalyst is sold to a reclaimer of precious metals in some instances.

Kerosene Hydrogen Treatment (8). The function of the kerosene hydrogen treatment is to remove sulfur from kerosene, saturate olefins, reduce gum formation, and remove aromatics. The kerosene is mixed with about 400 cu ft of hydrogen per barrel and heated in a fired heater to 400-800 F at 500-800 psi. It is then passed through a catalyst bed where the reaction occurs. The products are cooled, usually by heat exchange with the feed, and the excess hydrogen is separated and recycled. The products are reheated and steam stripped to remove hydrogen sulfide. A total of 4.9 million barrels per day (1971) of petroleum products are hydrogen treated. Most kerosene--1,000,000 bbl/day--is treated by a chemical sweetening process or by a hydrogen treatment. A total of 1,000,000 bbl/day of middle distillate stocks (mainly kerosene) are hydrogen treated. The treated kerosene is usually a refinery product or blended into a product. The hydrogen sulfide goes to gas processing.

Fired heaters require up to 70,000 Btu/bbl of kerosene treated. Since the reaction is exothermic, in some process variations all the necessary heat is supplied by the reaction. About 8 lb of steam per barrel are required for the stripping of hydrogen sulfide from the product. From 0.5 to 2 kwhr of mechanical energy per barrel are required to compress the hydrogen and to pump the feed through the system.

The emissions for this process are about the same as those for the Gasoline Hydrogen Treatment Process (7) except the internal between catalyst regeneration is weeks to months.

Gas-Oil Hydrogen Treatment (9). The function of the gas-oil hydrogen treatment is to remove sulfur from oils. The gas oil is mixed with from 750 to 1,500 cu ft of hydrogen per barrel and heated in a fired heater. The mixture then is passed through a catalyst bed where the reaction occurs. The pressures are from 500 to 800 psi. The products are cooled, usually by heat exchange with the feed, and the excess hydrogen is separated and recycled. The products are reheated and steam stripped to remove hydrogen sulfide. A Total of 4.9 million bbl/day (1971) of all petroleum products are hydrogen treated. The fraction of gas oil that is hydrogen treated is not known. However, at present, sulfur specifications in fuel oils are met by desulfurizing gas oil to a very low sulfur content and blending with residual oils. A total of 295,000 bbl/day (1973) of cat cracking feedstock (a part of gas oil) is hydrogen treated.(9) The treated gas oil may be catalytically cracked or blended into a fuel oil product. The hydrogen sulfide goes to gas processing.

The fired heaters require from 5,000 to 70,000 Btu/bbl. From 1 to 10 lb of steam per barrel are required for the stripping of hydrogen sulfide from the product. From 2.5 to 9 kwhr of mechanical energy per barrel are required to compress the hydrogen and to pump the feed through the system.

Emissions from this process are the same as those from the Kerosene Hydrogen Treatment Process (7).

Lubricating Oil Hydrogen Treatment (10). The function of the lubricating oil hydrogen treatment is to remove sulfur, hydrogenate olefins, remove gem forming compounds, improve color, and improve viscosity index of lubricating oils. The feed is mixed with 100 to 200 cu ft of hydrogen per barrel, heated in a fired heater, and is passed through a catalyst bed where the reaction occurs. The products are cooled, usually by heat exchange with the feed, and the excess hydrogen is separated and recycled. The oil is reheated and steam stripped to remove hydrogen sulfide. The fraction of lubricating oil that is hydrogen treated is not known. The hydrogen-treated oil is sent to lube oil processing for further treatment and the hydrogen sulfide stream is sent to gas processing.

Fired heaters require from 35,000 to 140,000 Btu/bbl of oil treated. From 15 to 30 lb of steam per barrel are required for the stripping of hydrogen sulfide from the product. About 2.5 kwhr of mechanical energy per barrel are required to compress the hydrogen and to pump the feed through the system.

Emissions from this process are essentially the same as those from the Gasoline Hydrogen Treatment Process (7).

Residual Oil Hydrogen Treatment (11). The function of the residual oil hydrogen treatment is to remove sulfur from the oil usually to about 0.3-0.5 percent concentration. The feed (3 to 5 hexant sulfur) is mixed with recycled hydrogen and from 400 to 700 cu ft of fresh hydrogen per barrel and heated in a fired heater to 650 -850 F. It then is passed through a catalyst bed where the reaction occurs. The pressure is about 1,000 psi. The products are cooled, usually by heat exchange with the feed, and the excess hydrogen is separated and recycled. The product is reheated and steam stripped to remove hydrogen sulfide. The first residual oil hydrogen treatment units are now going on stream and are fairly small. The desulfurized residual oil is blended into fuel oil. The hydrogen sulfide is further treated in gas processing.

Fired heaters require from 10,000 to 100,000 Btu/bbl. From 3 to 25 lb of steam per barrel are required to strip hydrogen sulfide from the product. From 1 to 4 kwhr of mechanical energy per barrel are required to compress the hydrogen and pump the feed through the system.

Emissions from this process are similar to the Gasoline Hydrogen Treatment Process (7) emissions.

Catalytic Hydrocracking (12). The function of the catalytic hydrocracking process is to convert a gas oil in the presence of hydrogen at 700-2,000 psi and 500-800 F into lighter, sulfur free, more valuable petroleum fractions. Catalytic hydrocracking generally opens the ring structure on polycyclic aromatics and naphthenes. Paraffins, single-ring naphthenes, and single-ring aromatics are resistant to hydrocracking. About 840,000 bbl/day (1972) of petroleum intermediates are hydrocracked.(9) Hydrocracking differs from hydrogen treatment in severity of treatment rather than type of treatment. The process variations are based on feed and catalyst used and include single or two-stage processes. The feed is usually a gas oil although occasionally residual oil or naphtha is fed. From 1,000 to 2,000 cu ft of hydrogen per barrel are consumed. The product from the reactor is separated by distillation into a wide range of sulfur-free hydrocarbons lighter than the feedstock and some hydrogen sulfide. Intermediate products are furnished to a variety of processes as indicated below.

Intermediate Product	Process to Which Furnished
Hydrogen sulfide	Gas processing
Hydrocarbon gases	Gas processing
Light naphtha	Blending into gasoline
Heavy naphtha	Catalytic reforming Blending into gasoline Blending into solvents
Kerosene	Blending into jet fuel
Gas Oil	Blending into fuel oil Blending into diesel oil Catalytic cracker Recycle
Residual	Pitch (product)

The oils produced by catalytic hydrocracking are sulfur-free saturated hydrocarbons which make then premium fuels for burning in jet engines and diesel engines, but poor fuels for automotive-type engines.

From 100,000 to 250,000 Btu of process heat per barrel from a fired heater are required to heat the reactor feed. About 18 lb of steam per barrel are required for stripping and 24 lb/bbl are generated in a waste heat boiler which cools the product. From 1 to 6 kwhr of mechanical energy per barrel are required for compression of the hydrogen and pumping of the feed and products through the process.

Atmospheric emissions--mainly carbon monoxide--result from regeneration of the catalyst. Since regeneration is infrequent (about 4 per year), the carbon monoxide produced should not be a problem. A liquid stream, mainly condensed steam with some H_2S, is drained from the stripper. The spent catalyst, a solid waste, is not produced in significant amounts because the catalyst life is several years. The spent catalyst is sold to a reclaimer of precious metals occasionally.

Gas Processing (13). The function of gas processing (frequently called the gas plant) is to stabilize light naphtha by removing gaseous hydrocarbons from it, and separate the various fractions of hydrocarbon gases. Amine stripping, which removes hydrogen sulfide from the gases, is sometimes considered part of gas processing although it is treated as a separate process in this study. In some refineries, gas-processing equipment is associated with each gas-generating process while in most new refineries gas processing is performed in a facility serving the entire refinery.

The separations are performed by a series of distillation and absorption operations, the number of operations being one less than the number of products. Gas processing can be a simple scheme producing fuel gases composed of butane and more volatile hydrocarbons, and a light naphtha; or a complex scheme producing methane, ethane, ethylene, propane, propylene, isobutane, butylene, butadiene, n-butane, isopentane, amylene, n-pentane, and a light naphtha.

The disposition of products and intermediate products is shown below.

Product	Use
Methane	Refinery fuel
Ethane	Refinery fuel Petrochemical feedstocks
Ethylene	Petrochemical feedstock Refinery fuel
Propane	LPG Petrochemical feedstock
Propylene	LPG Petrochemical feedstock Polymerization Alkylation
Isobutane	Alkylation
Butylene	Alkylation Polymerization
Butadiene	Petrochemical feedstock
n-butane	Isomerization Fuel Blend into gasoline

Product	Use
Isopentane	Blend into gasoline
Amylene	Alkylation Blend into gasoline
n-pentane	Isomerization Blend into gasoline
Light naphtha	Blend into gasoline Catalytically reform Blend into solvents Isomerization

Figure B-3 is a flow diagram for a plant of intermediate complexity which uses an absorption system. The gases from the refinery initially are compressed. The high-boiling petroleum gases and gasoline are absorbed in a heavy naphtha or kerosene. In the flow diagram, methane, hydrogen sulfide, and ethane pass from the top of the absorber de-enthanizer unit. The ethane and methane are stripped of hydrogen sulfide with diethanolamine and used for fuel gas. The propanes and less volatile components flow from the bottom of the absorber to the debutanizer where propane and butanes are separated from the gasoline by distillation. The depropanizer is another distillation column which separates butanes from propane.

Thermal energy is required for the distillation column and stripping the absorber solutions. This energy may be supplied by hot process streams from other processes rather than from a fired heater or steam. Mechanical energy, about 2 kwhr/bbl, is required to compress the gases for absorption as the distillation column normally operates under pressure.

The process is performed in a closed system and no emissions are generated.

Amine Stripping (14). The function of the amine stripper is to strip hydrogen sulfide from hydrocarbon gases by absorption in an amine solution. Sour gas from gas processing is the feed and the intermediate products are a sweet gas which is returned to gas processing and hydrogen sulfide which goes to the sulfur plant. The hydrocarbon gas containing hydrogen sulfide is contacted with an absorbent solution, such as

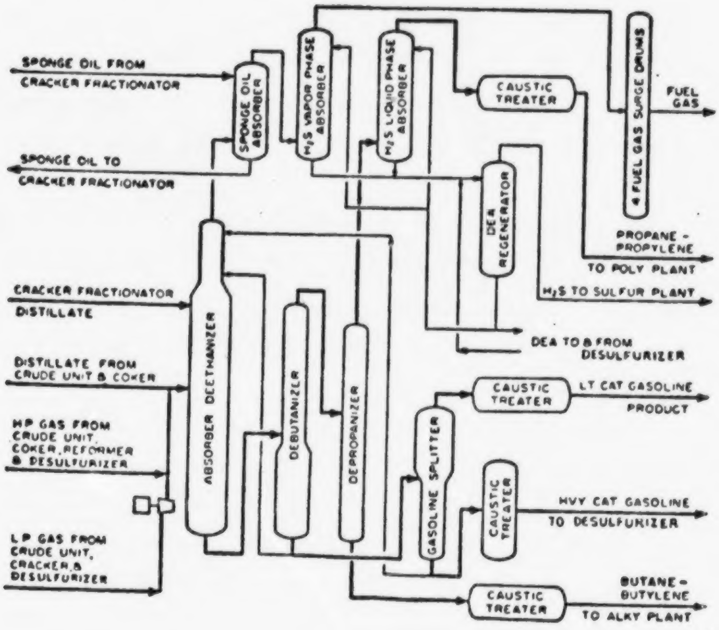
SPONGE OIL FROM CRACKER FRACTIONATOR
SPONGE OIL TO CRACKER FRACTIONATOR
SPONGE OIL ABSORBER
H₂S VAPOR PHASE ABSORBER
H₂S LIQUID PHASE ABSORBER
CAUSTIC TREATER
4 FUEL GAS SURGE DRUMS
FUEL GAS
DEA REGENERATOR
PROPANE - PROPYLENE TO POLY PLANT
H₂S TO SULFUR PLANT
DEA TO & FROM DESULFURIZER
CRACKER FRACTIONATOR DISTILLATE
DISTILLATE FROM CRUDE UNIT & COKER
HP GAS FROM CRUDE UNIT, COKER, REFORMER & DESULFURIZER
LP GAS FROM CRUDE UNIT, CRACKER & DESULFURIZER
ABSORBER DEETHANIZER
DEBUTANIZER
DEPROPANIZER
GASOLINE SPLITTER
CAUSTIC TREATER
LT CAT GASOLINE PRODUCT
CAUSTIC TREATER
HVY CAT GASOLINE TO DESULFURIZER
CAUSTIC TREATER
BUTANE - BUTYLENE TO ALKY PLANT

FIGURE B-3. STABILIZATION AND GAS RECOVERY SYSTEM(4) diethanolamine, in an absorption column to absorb selectively the hydrogen sulfide. Hydrogen sulfide is absorbed at a pressure of around 150 psi, and the absorbent solution is stripped at atmospheric pressure by boiling at the bottom of the stripper.

Thermal energy, about 1 lb of steam per lb of H_2S, is required to strip the hydrogen sulfide from the absorber solution. About 0.5 kwhr of mechanical energy per barrel is required to pump the liquids through the system.

No atmospheric emissions are produced. When diethanolamine is used as the absorbent solution, about 1 gallon of spent solution is drained per thousand barrels processed. However, since 10,000 to 20,000 gallons may be drained at one time, the impact on the sewage system of changing solutions may be severe. When monoethanolamine is used for the absorbent solution, about 1 lb of waste complex salts (solid) is removed from the system for each 3,000 barrels processed. No other waste is generated. The amount of waste is roughly proportional to the amount of hydrogen sulfide removed from refinery streams and, therefore, depends upon the amount of sulfur in the crude and the extent to which the products are desulfurized.

Sulfur Manufacture (15). Sulfur is manufactured in a Claus plant(6) as a method of disposal of hydrogen sulfide. About 1.2 million tons/year of sulfur is produced by the petroleum industry and this number is growing. The feed is hydrogen sulfide from the amine stripper. Where special market conditions exist, sulfur dioxide or sulfuric acid may be made using processes typical of the sulfur industry. As indicated by the flow diagram in Figure B-4, the hydrogen sulfide is burned with a substoichiometric quantity of air to make sulfur and water. The off-gas is cooled and the sulfur condensed as a liquid. About 60 to 70 percent of the sulfur is removed in the burner; the remaining hydrogen sulfide and sulfur dioxide gases are reheated and passed through a catalytic converter. The gases are cooled to condense liquid sulfur. In most systems, two to four converter stages in series are built into the system. Fifty to 60 percent of the remaining sulfur is removed in each converter stage. The total sulfur recovery in Claus plants varies from about 80 to 95 percent.

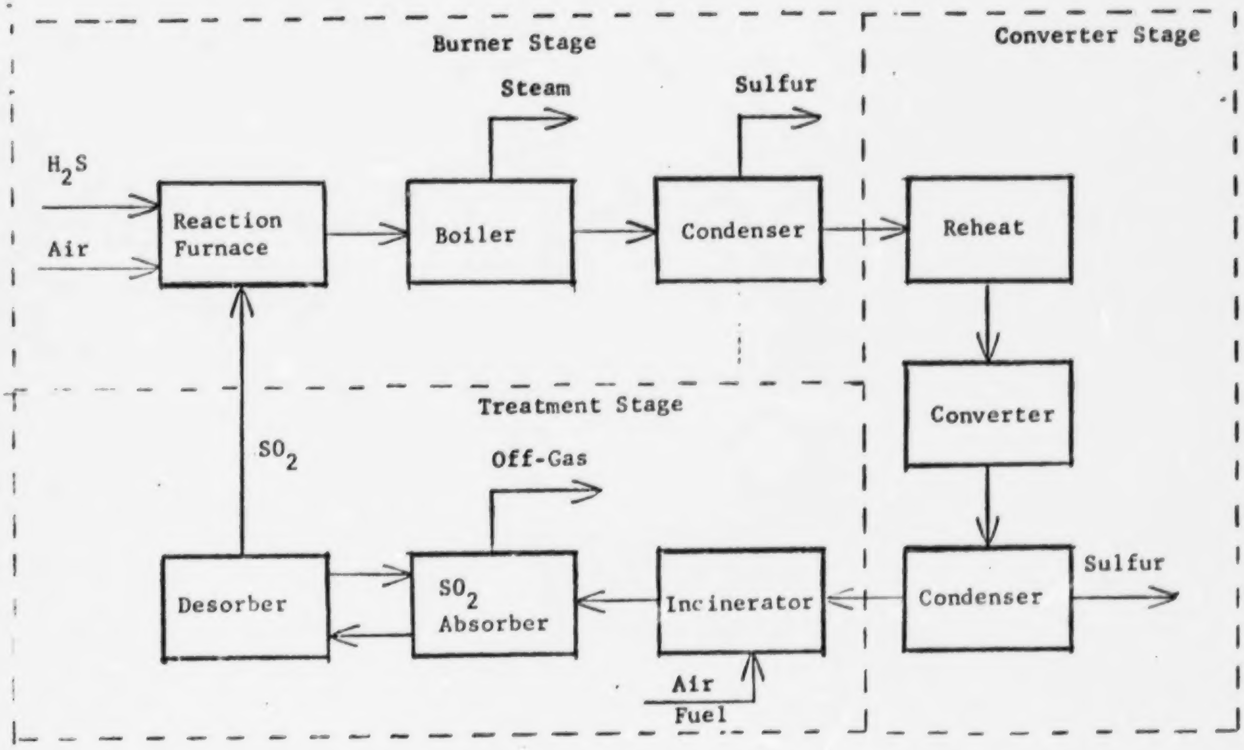
Burner Stage
Converter Stage
Steam
Sulfur
H_2S
Air
Reaction Furnace
Boiler
Condenser
Reheat
Converter
Treatment Stage
SO_2
Off-Gas
Desorber
SO_2 Absorber
Incinerator
Condenser
Sulfur
Air
Fuel

FIGURE B-4. CLAUS PLANT

Frequently, the tail gas from the Claus plant is treated to remove the last traces of sulfur-containing gases. The tail gas contains H_2S, SO_2, COS, and CS_2, compounds that have a disagreeable odor. In old plants they are incinerated to reduce the odor problem, although SO_2 emissions result from burning. Some new processes essentially add more converter stages to the Claus unit, other absorb the sulfur-containing off-gases, concentrate them, and recycle them to the Claus input, and still others oxidize hydrogen sulfide to sulfur in a wet process. While tail-gas treatment plants are being installed, long operating experience and standard design have not yet evolved. In the flow diagram (Figure B-4) the off-gas from the Claus plant is incinerated to convert all of the sulfur into SO_2 which then is absorbed. In the Wellman-Lord process for SO_2 removal and recovery a sodium sulfite solution is used for absorption while in other processes an amine solution is used. The clean off-gases are vented to a stack. The absorber solution is regenerated and the SO_2 is fed back into the Claus plant.

The Claus plant requires a fired heater, 400 Btu/lb of sulfur, to reheat the off-gases in the catalytic states, and a small amount of mechanical energy to move the gases through the plant. Steam, 4 lb per lb of sulfur, is generated in a boiler utilizing the heat content in the products of combustion following the burner stage.

The emissions from the Claus plant are primarily unconverted H_2S and SO_2. Hydrocarbons in the feed to the Claus plant form carbonyl sulfide and carbon disulfide which are also emitted. If the off-gas is incinerated, all sulfur compounds are converted to sulfur dioxide. Negligible liquid and solid wastes are generated. In a refinery where most of the sulfur in the crude is removed and collected as H_2S, the emissions from the Claus plant constitute the major sulfur emissions. As sulfur is removed from products and high sulfur foreign feedstocks replace sweet U.S. crudes, the emissions from the sulfur process will increase. A large 100,000-barrel-per-day refinery using a 1-percent sulfur feedstock removing sulfur from its fuel gases and desulfurizing many of its products and using an efficient Claus plant which converts 95 percent of the feed into sulfur, emits 5 to 6 tons of sulfur per day from the Claus plant. About 127,000 tons per year of sulfur dioxide are emitted from sulfur manufacture in all refineries.

Isomerization (16). The function of isomerization is to process normal butane, pentane, or hexane into the corresponding isoparaffin. Isobutane is used as a feedstock for alkylation. Isopentane and isohexane have a higher octane rating than normal pentane and normal hexane and are blended into gasoline. The process equipment consists of a heater, a reactor, and a set of distillation columns. The distillation columns frequently are shared with the alkylation process which uses the isobutane, or the distillation procedure may be included in gas processing. The reactor normally operates at 300 to 400 psi and at 400 to 500 F.

About 1.2 kwhr of mechanical energy per barrel is needed to pump the feed to the operating pressure. A fired heater (30,000 Btu/bbl) is used to heat the feed, and steam (20 lb/bbl) heaters are used to drive the distillation columns.

The process is closed and should have no gas emissions or liquid effluents in normal operation. The solid catalyst is replaced after about 2 years of operation. The spent catalyst is sold to reclaim its platinum value.

Catalytic Reforming (17). Catalytic reforming is used to convert low-octane naphtha into a high-octane gasoline, produce aromatics for the petrochemical industry, and to manufacture hydrogen. In 1971, about 3.2 million bbl/day of naphtha was reformed. The feed naphtha is reformed by passing it through a multiple-stage reactor with reheat between stages to maintain the temperature at 900-1100 F. Paraffins are dehydrogenated to naphthenes, naphthenes are dehydrogenated to aromatics, olefins are partially hydrogenated to paraffins, long and short chain hydrocarbons are cracked to gaseous hydrocarbons, and short chain hydrocarbons are isomerized. The process variations include methods of catalyst handling, different catalysts, and different operating conditions. One factor affecting process choice relates to product usage for either petrochemicals or gasoline. Another factor is the nature of the feedstock.

Reforming process throughput presently is 3.2 million barrels per day which makes it one of the very large volume processes in refineries. Additional facilities are being built rapidly because the reformer yields high-octane blending stocks used to minimize the need for lead additives.

In addition, the hydrogen from reforming is needed for the hydrogenation processes which remove sulfur from petroleum products. The reformer is a major user of energy in the refinery and the associated process heater is one of the larger heaters in the refinery.

The feed to the process is any desulfurized naphtha (sulfur poisons the catalyst). Heavy naphthas usually are fed when making gasoline, and light naphthas when making aromatics for the petrochemical industry. The products from the reformer are a high-octane gasoline or an aromatic petrochemical feedstock, propane, butanes, ethane, and 800-1500 cubic feet of hydrogen per barrel of feed. The gasoline has a clear (without lead addition) octane rating of 90-92 with existing units and 98-102 with new units and is blended with lower octane gasolines for sale. The propane is sold or used as fuel and the hydrogen is used for desulfurizing, hydrocracking, or for fuel.

The energy required by the process is 200,000 to 400,000 Btu/bbl and is supplied from a fired heater to heat and reheat the feedstock. From 3 to 6 kwhr are required for compression and to pump the fluids through the system. Usually no steam is used although a few processes use up to 30 lb of steam per barrel to heat the reboiler in a product fractionator.

The only atmospheric emissions are from regeneration of the catalyst. Usually the catalyst is regenerated by burning off carbon deposits at infrequent intervals; however, in some variations, the catalyst is continuously withdrawn from the reactor and regenerated. The major constituent of the emission is carbon monoxide at 0.002 to 0.02 lb/bbl (the amount of CO formed is independent of batch or continuous regeneration) or about 30 lb/hr in a large refinery that may typically reform 40,000 bbl/day. This is a very small source and is about equal to the emissions from a catalytic cracker with maximum controls and is less than the emissions from the process heater. Since the catalyst is mechanically stable and the feed is sulfur-free, very little particulate or sulfur emission is produced from catalyst regeneration. Because of the low emission rate, emission controls are not used. No liquid wastes are generated. The spent catalyst is a solid waste and may be processed for recovery of precious metal values or sent to a landfill. The amount of solid waste generated is small.

Fluidized-Bed Catalytic Cracking (18). The function of the catalytic cracking process is to convert distillate oils into high-octane gasoline, raw materials for alkylate production, petrochemical raw materials, heating and diesel oils, and liquefied petroleum gases. About 3.9 million bbl/day (1971) of oil is fed into fluid-bed catalytic crackers not including a 22 percent recycle. Two major process variations are the fluidized bed and the moving bed. Since the emissions from the two systems are different, they are discussed separately in this report. The fluidized-bed units are built in sizes up to 75,000 bbl/day with 40,000 bbl/day being typical.

In the fluidized-bed catalytic cracker, hot gas oil is fed into a line at the bottom of the reactor where it mixes with the catalyst. The gas oil is cracked as it passes up through the reactor. The cracked products leave the top of the reactor, are cooled, and fractionated in a distillation column associated with the reactor into the product streams. In a single pass, 50 to 80 percent of the feed is converted into lighter hydrocarbons. Some or all of the unconverted gas oil may be recycled. The catalyst flows to the regenerator where the carbon is burned off with air. In about 50 percent of the units, the flue gas is burned in a carbon monoxide boiler, while in others the CO-rich flue gas is emitted to the atmosphere.

The major process variations involve catalyst handling and reactor design. In one variation, the reaction takes place in the riser line which becomes the reactor. In another variation, the recycle and virgin feed are reacted in different risers to obtain a more severe treatment of the recycle oil.

The feed to the catalytic cracker may be any hydrocarbon stock from kerosene to vacuum gas oil or deasphalted residual oil. The feed is usually the distillate oils from the crude and vacuum stills, the heavy oils from coking and hydrocracking, and a large recycle heavy oil stream.

A complete range of petroleum products is made in the catalytic cracker and a large distillation column is associated with the cracker to separate these components. The amount of each product can be varied by changing operating conditions. The coke deposited on the catalyst is burned during regeneration to supply some of the heat required by the process. The products and their special characteristics and uses are listed below.

Gases	Rich in isomers and olefins	Further processed in gas processing
Naphtha	Rich in high-octane components	Blend into gasoline
Light oils	--	Fuel Recycle
Residual	--	Fuel Recycle

Incidental to the process, the sulfur concentration in the light and residual product oils is reduced to about 50 percent of the concentration of sulfur in the feed. The partial desulfurization makes these oils more desirable fuels. In addition, the product oils are more easily desulfurized than the feed oil.

Thermal energy (up to 70,000 Btu/bbl) may be used to preheat the feed. Steam (about 40 lb/bbl) is used to strip the spent catalyst and fractionate the product. Mechanical energy (0.3-4 kwhr/bbl) is used to drive the air blowers and feed pumps. The flue gases are usually cooled by heat exchange in a boiler, and the carbon monoxide is burned in a boiler. The amount of steam generated (about 110 lb/bbl) may be greater than the steam used.

The flue gas (about 2,000 cu ft/bbl) from the catalytic cracker is a major atmospheric emission from a refinery. The flue gas is a mixture of carbon monoxide and nitrogen with traces of hydrocarbon and sulfur compounds and, in the absence of a carbon monoxide boiler, contains most of the carbon monoxide emitted by a refinery. At present, almost all of the 4.5 million tons per year of carbon monoxide emitted by catalytic crackers comes from units without CO boilers. The volume of stack gas from a catalytic cracker is similar to that from a large industrial boiler or a small electric-generating boiler. In a fluidized-bed catalytic cracker the catalyst is in the form of a coarse powder and the action of the fluid-bed grinds the powder into a fine dust, some of which passes through the dust-collection system. This dust is a major source of particulate emission (33,000 tons per year*) from refineries. About 5 percent(8) of the sulfur in the feed deposits in the coke on the catalyst and the sulfur is oxidized in the regenerator and leaves in the flue gas.

Analyses of the stack gas show that 15-60 percent (usually 30-50 percent) of the sulfur(12) is emitted as SO_3 and the remainder as SO_2. Thus, the catalytic cracker is a major sulfur emitter (333,000 tons per year as SO_2*) in refineries. Hydrocarbons (165,000 tons per year*) and nitrogen oxides (50,000 tons per year*) are emitted in significant amounts by catalytic crackers. A liquid waste stream from the fractionator is the condensed steam from the process. This water is sour and is combined and treated with other sour waters before release. About 0.1 lb of catalyst is used per barrel of feed, so that about 2 tons per day of solid waste are generated by a 40,000-bbl/day unit.

A variation in refinery operation which may reduce the atmospheric emissions of SO_2 is desulfurization of the feed to the catalytic cracker. This change has been made in some refineries for economic reasons, and it has been suggested as a general method of meeting anticipated sulfur dioxide limits on the regenerator stack gas. Caustic scrubbing of the regenerator gases also has been suggested and Exxon plans to install a sodium carbonate scrubber in a refinery where disposal of the sodium sulfite solution generated will not be a problem.

Moving-Bed Catalytic Cracking (19). The function of the moving-bed catalytic cracking is the same as fluidized-bed catalytic cracking. 510,000 bbl/day are fed into moving bed catalytic crackers not including a 20-percent recycle. The feeds and products are also similar. The moving-bed units are generally smaller than the fluidized-bed units. Large units may process up to 35,000 bbl/day and 15,000 bbl/day units are typical. The catalyst is in the form of beads, 1/8 to 1/4 inch in diameter. The catalyst is added continuously to the top of the reactor, flows through the reactor and regenerator by gravity, and is removed from the bottom of the regenerator. An airlift station elevates the catalyst from the bottom of the regenerator to the top of the reactor. The hydrocarbons flow down through the reactor and the combustion air can flow up or down through the regenerator depending upon the particular process variation. CO boilers have not been used in moving-bed crackers.

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* Calculated from throughput and emission factors.

Thermal energy (100,000-300,000 Btu/bbl) is required to heat the charge to reaction temperature. More heat is required than in the fluidized-bed process because less heat from hot regenerated catalyst is available. Steam (100 lb/bbl) is required by the fractionator and to seal the gases in the reactor from the gases in the regenerator. Mechanical energy (0.1-1.5 kwhr/bbl) is required for blowing air into the regenerator and for pumping oil. Steam (160 lb/bbl) can be generated by the hot off-gas from the regenerator.

The emissions from the moving-bed cracker are less than from fluidized-bed system, primarily because of the smaller size of the moving-bed units. The catalyst perticles are larger and less dust is generated. Slightly less carbon deposits on the particles in the bed so that less carbon monoxide and sulfur dioxide are emitted. Hydrocarbon and nitrogen oxide emissions are small. The wastewater quantity is about the same as the steam used. The water is sour and is treated before release. The spent catalyst from the process is a solid waste and amounts to 0.1 to 0.2 lb/bbl. In a large unit, this amounts to more than a ton per day.

Visbreaking (20). The function of visbreaking is to thermally crack residual oils into a lighter oil under mild conditions (850-890 F). The residual oil is passed through a heater to crack it and then fractionated in atmospheric and vacuum towers. About 230,000 bbl/day (1971) of residual oil are visbroken and a similar amount of gas-oil is thermally cracked in a similar process (not shown in flow diagram). The light oil product is used to cut (dilute) the vacuum residue from the visbreaker which is then sold for heavy fuel oil. The light product is sometimes used as a feed to a catalytic cracker. Visbreaking is more typical of foreign refineries than American refineries.

The main energy requirement is 260,000 Btu/bbl from a fired heater to crack the oil. Mechanical energy (1.8 kwhr/bbl) is needed to pump the oil. Steam (100 lb/bbl) is generated by cooling and condensing the cracked oil and about 20 lb/bbl are used in the fractionating tower.

Since the process is closed, no atmospheric emissions are produced. Water from fractionation is treated with other sour water. No solid waste is generated.

Coking (21). The function of coking is to crack heavy residuals into a full range of hydrocarbon products and to produce petroleum coke. About 20 percent of the feed is converted into coke (42,000 ton/day). Most coking processes are closed, although about 10 percent of coking is performed in a fludized-bed process (an open process) where combustion of some of the coke is used to supply the process heat. The off-gas from the combustion chamber in a fluidized-bed process is burned in a CO boiler and emitted to the atmosphere.

In a closed, drum-coking process, the oil is heated to 900-930 F and then passed into a coking drum where it is cracked into lighter hydrocarbons and coke. Normally two coking drums are installed and one is used while the other is emptied. The volatile hydrocarbons are fractionated. In the open, fludizing-coking process, hot oil is cracked in a reactor containing a bed of coke at 930-950 F. The heat for the process is supplied by burning part of the coke in a second fluidized bed called the burner where the coke is heated to about 1100 F. The off-gas from the burner is oxidized in a CO boiler to remove CO and conserve heat.

The feed to the coker is usually a heavy residual oil from the vacuum still or the catalytic cracker, or a deasphalted oil from asphalt manufacture. The products of the coker are a wide range of hydrocarbons similar to the products of catalytic cracking and are used similarly. About 20 percent of the feed is converted into coke which is burned as fuel or sold to make carbon electrodes.

In the drum coking process, from 300,000 to 400,000 Btu/bbl are used to heat the feed in a fired heater. In the fluid coker this heat is supplied by burning coke rather than using a fired heater.

About 80 lb of stem per barrel are used in the fractionator and 180 lb of steam per barrel are generated by cooling the hot products of coking. Thus, the process generates 100 lb of steam per barrel. Mechanical energy (1.5 kwhr/bbl) is needed for high-pressure water jets to wash the coke from the drums, for compressing air, and to pump fluids through the process.

No atmospheric emissions are produced in the drum-coking process. In the fluidized coking process, the thermal energy is supplied by burning the coke to carbon monoxide. The carbon monoxide may be used in a boiler associated with the process or used for fuel at other places in the refinery. About 5 percent of the carbon in the feed is burned and emissions are typical of this combustion. Presumably the sulfur content of the feed would be distributed in a manner similar to a catalytic cracker where the sulfur concentration in the coke is slightly less than the sulfur concentration in the feed. Therefore, 3-5 percent of the sulfur in the feed would be emitted with the product of combustion. Both coking processes fractionate the product and the steam used for stripping is condensed and sent to the sour-water stripper. In the drum-coking process, high-pressure water jets are used to break the coke from the drums and the water from these jets goes into the plant sewers. No solid wastes other than coke dust is generated.

Polymerization (22). The function of the polymerization process is to produce a high-octane gasoline or petrochemical feedstocks from olefin gases. It is used in some refineries in place of isomerization and alkylation (the generally preferred process). The olefins are passed over a catalyst such as phosphoric acid at 500 psi and 275-375 F. The feedstock is an olefin stream of ethylene, propylene, butylene, and/or amylene from gas processing. The products are high-octane gasolines or petrochemical feedstocks and petroleum gas which is used for fuel.

Energy from a fired heater is required only on startup because the reaction is exothermic and the feed is heated by heat exchange with the product. Steam (20 lb/bbl) is used for fractionation of the product. Mechanical energy (1.2 kwhr/bbl) is required to pump the feed liquid.

Since the process is closed, there are no atmospheric emissions. Phosphoric acid is a liquid catalyst which may be washed from the reactor during a maintenance operation. Sometimes the phosphoric acid is absorbed on a solid support and the support and acid is sent to a landfill when the catalyst is replaced. The quantities of liquid and solid waste are not significant.

Alkylation (23). The function of alkylation is to synthesize high-octane gasoline by reacting olefins, such as butylene, with isobutane. 812,000 bbl/day (1972) of alkylate is produced. In other processes, perhaps more typical of the petrochemical industry, benzene is alkylated with ethylene or propylene to make petrochemical feedstocks. Anhydrous hydrofluoric acid or sulfuric acid is the catalyst used. The feedstock is an olefin and isobutane from the isomerization process and/or gas processing. Previously, only butylene was used, but now propylene and amylene are often alkylated. The product is high-octane gasoline. Propane is an undesired diluent in the feed and is a product of the fractionating tower associated with alkylation. Since the alkylation process is one of the few processes capable of yielding high-octane unleaded fuel, it is being installed in numerous refineries and present capacity is increasing.

Two process variations are employed: a sulfuric acid catalyst (536,000 bbl/day); or an anhydrous hydrofluoric acid catalyst (276,000 bbl/day) (1972)$^{(9)}$. The major difference is in temperature of operation (80 F for the hydrofluoric-acid process, and 45 F for the sulfuric-acid process). Hydrofluoric acid is regenerated in the process by fractionation while sulfuric acid is regenerated outside of the process.

Energy from fired heaters is not required. Steam (100-300 lb/bbl) is needed to fractionate the intermediate product. The quantity of steam required is large because the recycle isobutane stream must be fractionated from n-butane, a diluent. Mechanical energy (0.5-5 kwhr per barrel) is required to compress the feed and recycle gases, and in the sulfuric acid process for refrigeration.

No atmospheric emissions are produced. About 17 lb of 90 percent sulfuric acid per barrel are wasted from the sulfuric-acid process. The sulfuric acid is returned to the sulfuric acid plant for regeneration. The feed acid strength is about 98 percent. The products, when using either catalyst, are given a caustic wash and 20 lb of spent caustic solution per barrel are disposed of. No solid waste is produced.

Lube Oil Processing (24). The function of the lube oil process is to make a lube oil stock suitable for blending into lubricating oils from selected distillate and residual feedstocks. Widely differing processes are used depending upon the feedstock, the ultimate use, and the period of equipment installation. In the traditional process, the feed oil is contacted with sulfuric acid which reacts with unsaturates and polyaromatics and forms a sludge. The sludge is removed by filtration with clay.

Another process (Duol-Sol) employs two solvents: propane which selectively extracts paraffinic hydrocarbons (lube oils) and rejects asphaltic hydrocargons, and cresylic acid which preferentially dissolves asphaltic and naphthenic hydrocarbons. The two solvents flow in a countercurrent manner through a series of extraction stages. The feedstock is introduced near the middle of the unit. The solvents are removed by distillation from the lube oil and asphalt.

After removal of asphalt, selective solvents and refrigeration are used to separate waxes from lubricating oils. In one dewaxing operation, propane is added to reduce the viscosity of the oil, the oil is chilled to below its lowest anticipated operating temperature, and wax is crystallized out and separated by filtration.

The preferred lubricating oils are a high-boiling paraffin with several side chains. Normal paraffins are unsatisfactory components for low-temperature operation because of their high melting point. Naphthenic compounds can be used only within a narrow temperature range because their viscosity changes rapidly with temperature. Polyaromatics and unsaturated compounds form sludges and varnishes when present in lubricating oil and, therefore, are unsatisfactory. Therefore, the preferred feedstocks is an oil rich in paraffins and lean in other hydrocarbons.

The products of lube oil processing are lubricating oils (which are blended into the many different lubricants), waxes, fuel oil, and asphalt.

Lube-oil processing is a large source of sludges in a refinery. The used clays from filtration represent a major solid waste. The oils are washed with caustic solutions at various points in the process, thus generating a liquid waste stream. The lube-oil process is a major user of steam and mechanical power in the refinery.

Fired heaters are not usually used in processing lube oils. Depending upon the process, 100 to 400 lb of steam are required per barrel, primarily for separation of solvents. Mechanical energy requirements are large (2 to 10 kwhr/bbl) for refrigeration and pumping the oil through filters.

Lube-oil processing is not a major source of air emissions. In some processes the oil is blown with air, but since the boiling point is high, no serious emission occurs. In other processes a decolorizing clay is regenerated by burning the sludge adsorbed on it, producing small atmospheric emissions.

The liquid waste from the process is condensed steam from the solvent stripping which is pure. The sludge from the acid-clay process is frequently burned in the refinery boiler. The clay is a solid waste. In at least one lub-oil refinery the sludge was lagooned and stored until the lagoon accidentally ruptured creating water pollution.

Replacement of the acid-clay process with a solvent process reduces the amounts of sludge formed.

Asphalt Production (25). The function of the asphalt process is to make asphalts from residual oils of asphalt-based crudes. About 644,000 bbl/day (1972)(2) of asphalt is produced. Asphalt is high molecular-weight hydrocarbon containing polycyclic aromatic rings. Some residual oils have the desired properties and require no treatment. In others, the asphalt stock is oxidized to increase the melting point by blowing air through the residual oil. During air blowing, the residual oil is heated to about 500 F. The reaction is exothermic and after initial heatup, additional heat is not necessary. Air blowing is stopped when the asphalt reaches the proper consistency. Other asphalts are produced by mixing the feedstock with propane followed by separation of a solid asphalt fraction and a liquid nonasphalt fraction. The products are sold to the various asphalt-based industries, such as roadbuilding, roofing paper, and sealant manufacture.

Energy from fired heaters (100,000 to 300,000 Btu/bbl) is required in the solvent process primarily for stripping the solvents from the asphalt and the deasphalted oil. About 5,000 to 10,000 Btu/bbl are needed in the air-blowing process to heat the feedstock to the reaction temperature. Fifty pounds of steam per barrel are used to strip the solvent in the solvent process. If most of the energy is derived from fired heaters, little is needed from steam and vice versa. Mechanical energy (0.1 to 3 kwhr/bbl) is required for the solvent process mainly for agitation of the extractor stages. About 1 kwhr/bbl is needed to compress air for the air-blowing reaction.

The solvent process is closed and no atmospheric emissions are formed. While the air-blowing process emits gases to the atmosphere, the quantity is small since the asphalt previously has been distilled at a high temperature. Sometimes air-blowing produces an obnoxious odor and the off-gas is used for combustion air in a nearby heater. The condensed steam from the solvent stripping operation is a wastewater stream. No solid waste is produced.

Storage and Blending (26). The function of storage and blending is to store intermediate products and to mix or blend the various intermediate products into final products. The materials are stored in large tanks, which are pressurized for liquefied gases, specially vented for liquids with high vapor pressure, specially constructed for materials of moderate vapor pressure, and vented for materials of low vapor pressure. Liquids are blended in a blending tank by agitation. Essentially all raw materials, intermediate products, and products are stored in tanks. Most products are a blend of several intermediate products and perhaps purchased raw materials.

No fired heater is used with blending and storage. A negligible amount of steam is used to heat tanks containing heavy residual oils. A negligible amount of mechanical energy is required for pumping and agitation.

Hydrocarbon emissions from storage vessels depend on three basic mechanisms: breathing loss, working loss, and standing storage loss. Breathing and working losses are associated with cone-roof tanks and standing storage losses are associated with floating-roof tanks.(7) Breathing losses are hydrocarbon vapors expelled from the vessel by expansion of existing vapors due to increases in temperature or decreases in barometric pressure. Working losses are hydrocarbon vapors expelled from the vessel during emptying or filling operations. Emptying losses result from vapor expansion caused by vaporization after product withdrawal. Filling losses are the amount of vapor (approximately equal to the volume of input liquid) vented to the atmosphere by displacement. Breathing and emptying losses are usually restricted to fixed-roof tanks vented at atmospheric pressure. Filling losses are experienced in fixed-roof tanks and low-pressure storage tanks vented to the atmosphere. Both working losses and breathing losses can be significant. Standing storage losses from floating-roof tanks are caused by the escape of vapors through the seal between the floating roof and the tank wall, the hatches, glands, valves, fittings, and other openings. The magnitude of hydrocarbon emissions from storage vessels depends on many factors including the physical properties of the material being stored, climatic and meteorological conditions, and the size, type, color, and condition of the tank.

The annual hydrocarbon emissions from crude oil, gasoline, and distillate tanks are estimated at 1.3 million tons. At present, 75 percent of these tanks are equipped with floating roofs. The annual estimated emissions constitute about 3 percent of the total national hydrocarbon emissions and about 7 percent of the 18.6 million tons/year emitted from all stationary sources. Minor liquid and solid waste quantities are generated by maintenance operations.

Prime Movers (27). The function of the prime mover is to supply mechanical energy to pumps, blowers, compressors, etc. About 7.5 kwhr of mechanical energy are required per barrel of crude processed in a modern refinery. Electrical drives are usually the most convenient, especially for smaller units. For large units, steam turbines are typical; gas turbines or internal combustion engines occasionally are used. On some equipment more than one drive is installed to assure continuous operation. For example, an electric motor and a steam turbine may drive the same pump, one unit being used normally and the other unit being on standby in case of failure of the primary driver. The steam turbine is especially applicable in a refinery since steam is normally distributed at about 400 psi and used at 175 or 30 psi. A steam turbine is used both to supply mechanical energy and low-pressure steam to a process.

Electricity and steam are secondary sources of power and the fuel is burned at a place remote from the process using the energy. A gas turbine would burn either refinery gas or natural gas and a diesel engine would use a diesel oil.

The process emissions are typical of drives and not peculiar to the refining industry. Since most drives are steam or electric, the emission relating to the mechanical energy is at the site of steam or electric generation and not at the process site.

Steam Generation (28). The function of steam generation is to supply steam to the various processes for direct use in the operation, for heating, and to drive steam turbines. Frequently, steam is used for electric power generation. Overall about 30 to 100 pounds of steam are used per barrel of crude oil processed at a refinery. In a refinery processing about 100,000 barrels of oil per day, about 250,000 lb/hr of steam are used. If the refinery generates its own electricity (not usual practice), the boiler is typical of one used in the electric power industry and probably operates at a steam pressure of 1000 psi or higher. Steam for distribution at 500, 175, and 15 psi is supplied from bleeds off the turbine driving the electric generator. If the refinery does not generate electricity, steam is generated at about 500 psi in a boiler typical of large industrial boilers. Steam for distribution at 175 and 15 psi is obtained by reducing the pressure of 500 psi steam and from steam turbines exhausting at the lower pressures. In addition to generation in the main boiler, steam is generated by boilers in several of the processes. The largest steam generator associated with a process is the carbon monoxide boiler on the exhaust from the catalytic cracker. Waste-heat boilers may be placed in the flue gas streams for process heaters. In some processes, the process fluids are cooled by generating steam. Most of these boilers would generate steam at one of the lower distribution pressures.

A steam generator is used as an incinerator for combustible liquid and solid wastes. Spilled oil, sludges, and residues from maintenance operations such as tank cleaning are usually incinerated in a steam generator.

Table B-4 lists the amounts of the different fuels used at refineries. Most of the nongaseous fuels and some of the gases would be burned in the steam generators. From 10 to 20 percent of the fuel used in a refinery is burned in the steam generator. Also while the industry average energy demand is 700,000 Btu/bbl, many newer complex refineries use only 500,000 Btu/bbl.

The process emissions from the steam generator are typical of conventional steam generators and the fuel used. In the past, various oily wastes, sour gases, and high sulfur oils have been burned in the steam generator, but since pollution control regulations are becoming more stringent, the use of such fuels is decreasing. Liquid wastes are generated by treating boiler feed water but present a minor problem. Solid wastes include ash from the fuels such as acid sludge and coal, and sludges from treatment of boiler feed water.

Process Heaters (29). The function of the process heaters is to heat various process streams. Most of the fuel used in a refinery is burned in process heaters. Steam heaters can be used at operating temperatures up to about 400 F and above that temperature fired heaters are required. In addition, superheated steam is required by a few processes and the steam usually is superheated in the fired heater associated with that process. A pipe heater, as shown in Figure B-5, is the standard fired

TABLE B-4. REFINERY FUEL AND ENERGY SOURCES (1969)(10)

Fuel	Quantity/year	10^{12} Btu/year
Fuel Oil, 1000 bbl	43,323	263
Acid Sludge, 1000 bbl	95	0
Coal, 1000 tons	570	14
Natural Gas, MMcf	997,886	998
Refining Gas, MMcf	984,561	1,000
Petroleum Coke, 1000 tons	10,625	320
Purchased Electricity, MMkwhr	17,927	61
LPG, 1000 bbl	6,620	25
Purchased Steam, MMlb	24,396	27
Total Energy Equivalent, 10^{12} Btu	-	2,728
Crude Oil Run to Stills, MMbbl	3,880	-
Energy Consumption, Btu/bbl of Crude Oil	703,000	-

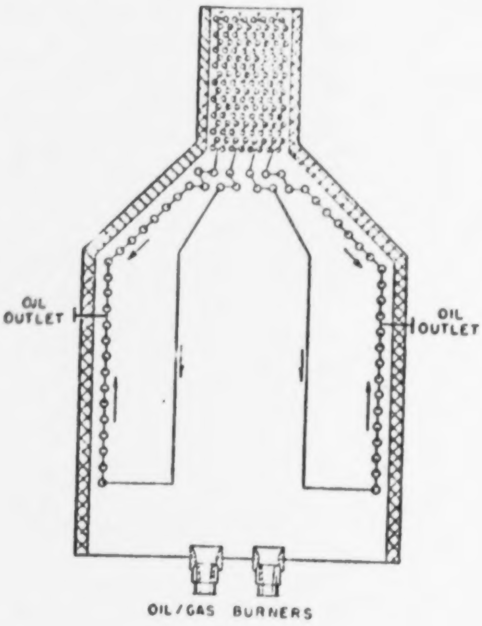
OIL INLETS
OIL OUTLET
OIL OUTLET
OIL/GAS BURNERS

FIGURE B-5. PIPE HEATER(4)

heater in the petroleum industry. In this heater, liquid petroleum passes through tubes exposed to a hot combustion zone. The oil enters at the top of the heater and is heated convectively and countercurrently by the flue gases. The oil is then passed into the tubes on the side walls of the furnace where it is heated by radiation. Steam superheater tubes, if any, are placed at the top of the furnace just below the oil tubes. The process heater on the crude still is larger than most industrial boilers and in the largest still is comparable in size to the steam boiler for a 100 megawatt electric generator. The heaters for catalytic reforming, catalytic cracking, and coking compare in size with large industrial boilers. In processes with less throughput, the units may be fairly small and compare in size to a package steam boiler.

Most process heaters are equipped to burn gas or oil or both. The pipe heater usually cannot be adapted easily to solid fuels.

The emissions from the pipe heater are those typical of industrial boilers. Particulate emissions result from ash in the fuel and unburned carbon that pass through the furnace. Hydrocarbon emissions result from incomplete combustion. Sulfur dioxide is formed from the sulfur in the fuel. Nitrogen oxides are formed by reaction with N_2 in air at the high combustion temperature. Carbon monoxide is formed because of incomplete combustion of the carbon in the fuel. Each of these emissions is at a low concentration but the total represents a major emission because of the large amounts of fuel burned. Table B-5 lists estimated emissions from combustion sources calculated from emission factors(11) and fuel consumed in the petroleum refining industry.

TABLE B-5. ESTIMATES OF ATMOSPHERIC EMISSIONS FROM COMBUSTION SOURCES IN PETROLEUM REFINING INDUSTRY (1969)

Emission Type	Emissions, 1,000 short tons/year
Particulate	60
Sulfur dioxide	270
Carbon monoxide	1.9
Hydrocarbons	42
NO_x	500

WASTE CONTROL METHODS

In addition to specific control devices associated with particular processes, the refinery employs emission control equipment that services the entire refinery--for example, flares for control of atmospheric emissions, and water treatment facilities for wastewater. As indicated previously, the steam generator usually is used to incinerate combustible wastes.

Flares

The function of the flare is to burn gases released in emergency situations from any process in the refinery. In the past, flares have been used to burn unwanted gases, but at a modern refinery, combustible gases are used for their fuel value. Flares also had been used to vent and incinerate sour and malodorous gases, but pollution control regulations have reduced this practice. At the present time, if an equipment malfunction requires an emergency reduction in pressure in a large process vessel, the gases are vented to a flare to eliminate fire hazards. A flare consists of a burner, pilot light, and air injection system. Excess process gases are sometimes vented to the flare at a very high rate and for short times more gas may be burned in the open or a stack might be built around the flare to reduce light and noise and to prevent hazards to nearby process equipment.

The flare requires a small pilot flame and steam to promote smokeless combustion.

The atmospheric emissions caused by a flare depend upon the gas vented; for example, sulfur in the gas will form SO_2. A modern flare is smokeless, and particulates, carbon monoxide, and hydrocarbons are not emitted in quantity. Since the flare is a flame device, NO_x is undoubtedly made and emitted. The total quantity of materials flared over a period of a year is small; therefore, the emissions from the flare should be small. However, large quantities occasionally are flared which may cause a temporary air pollution problem.

Wastewater Treatment

Wastewater treatment removes impurities from water effluents. A refinery produces many types of wastewater streams such as used process and cooling water, storm drainage, and sanitary sewage. Much of the waste process water is contaminated with hydrogen sulfide and other compounds with obnoxious odors. This sour water is boiled and treated with acid to remove hydrogen sulfide in a sour-water stripper. The sour-water stripper is usually a packed tower perhaps 10 feet in diameter and 30 feet or more high. About 10 gallons of sour water are treated per barrel of oil processed. The products are sweet water and hydrogen sulfide gas (the latter is sent to a Claus plant).

Storm drainage and process water are usually sent through an API oil-water separator which decants the oil from the water. The API separator is a large item of equipment.

Sanitary sewage and any high BOD process water would be treated in a biological treatment plant similar to a sewage plant for a small city.

The energy requirements for water treatment are small except for steam used by the sour-water stripper. It uses about one pound of steam per gallon of water treated.

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APPENDIX C

THE SECONDARY NONFERROUS METALS INDUSTRIAL PROCESS PROFILE

INDUSTRY DESCRIPTION

The history of the metals recycling industry can be traced back to antiquity. Records of ancient peoples give evidence of crude melting techniques that existed at the dawn of civilization. Archaeologists believe the rudimentary recovery of iron, lead, and copper occured in earliest times.

But, recycling, as we know it today, is the development of the past 100 years. During this period, scientific and sophisticated technology has been developed to transform waste material into valuable products. More significantly, the volume of scrap expanded with the growth of industrialization, particularly in the United States, which, today, has the largest and most effective recycling industry in the world.

More than 3 million tons of nonferrous scrap metals are recovered annually by secondary smelters, refiners, ingot manufacturers, fabricators, foundries, and other industrial consumers in the United States. In its total operation of metallics, the U. S. recycling industry is an $8 billion industry,* occupying a major role in the economic life of the country. And the growth potential of the secondary industry is substantial.

In recent years the concept of recycling has come to the fore impelled by increased concern for the environment, the awareness of dwindling natural resources, and the realization that solid waste accumulations could choke urban society. Recycling does represent the most affirmative environmental response and a highly constructive economic response to the critical challenge of solid waste disposal.

Furthermore, various studies have indicated that the world's resources are fast being depleted. Obviously, recycling must play a major role in future conservation considerations.

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* Fine, P., Rasher, H. W., and Wakesberg, S., Operations in the Nonferrous Scrap Metal Industry Today, published by NASMJ, New York, New York (1973).

The companies that make up the secondary nonferrous metals industry are generally small and generally are not well equipped to deal with the development and application of new technology for the control of pollution. They lack the needed technical capabilities and financial resources. However, they are concerned about the environment and are making efforts to reduce the pollution potential of the industry. These efforts could be accelerated by partial support through demonstration projects from the government, since such support might encourage industry to undertake additional work.

DISCUSSION OF SECONDARY NONFERROUS METALS INDUSTRIAL PROCESS PROFILE

The Secondary Nonferrous Metals Industry consists of what may be considered for purposes of this analysis to be industry "segments" that convert scrap metals or waste materials to products that are marketed for use or consumed in the form they exit from the process. Each segment is comprised of companies that are considered competitors in the production of the same products. The secondary industry and each segment of the industry have an identifiable population of companies and have a degree of commonality with respect to raw materials consumed, process employed, products produced, environmental control problems, pollutants produced, and control equipment used.

Detailed description of the processes for each segment follows.

Segments

The Secondary Nonferrous Metals Industry consists of about 20 segments. The major segments in regard to volume of metal recovered from scrap are:

(1) Copper Segment
(2) Brass and Bronze Segment
(3) Lead Segment
(4) Aluminum Segment
(5) Zinc Segment

The minor segments are:

(1) Tin
(2) Nickel
(3) Cobalt
(4) Magnesium
(5) Mercury
(6) Antimony
(7) Precious Metals
(8) Titanium
(9) Selenium
(10) Cadmium
(11) Germanium
(12) Hafnium
(13) Zirconium
(14) Indium
(15) Beryllium

Major Companies

The Secondary Nonferrous Metals Industry encompasses a host of companies. For example, in 1973, there were 125 companies producing secondary aluminum, 130 companies producing secondary lead, and 44 companies producing secondary copper and brass and bronze products. The size of these companies ranges from small family-owned facilities to large corporations. The major companies are identified at the end of each segment description which follows.

These companies are found throughout the United States. However, in most cases, as noted in Figures 1, 2, 3, and 4, which show the major location of secondary aluminum, zinc, copper, and lead segments, they are found in the vicinity of populated areas where the scrap generally is found.

Manufacturing Operations

Manufacturing operations fall into 3 basic categories: (1) scrap pretreatment, (2) smelting/refining, and (3) casting (product formation).

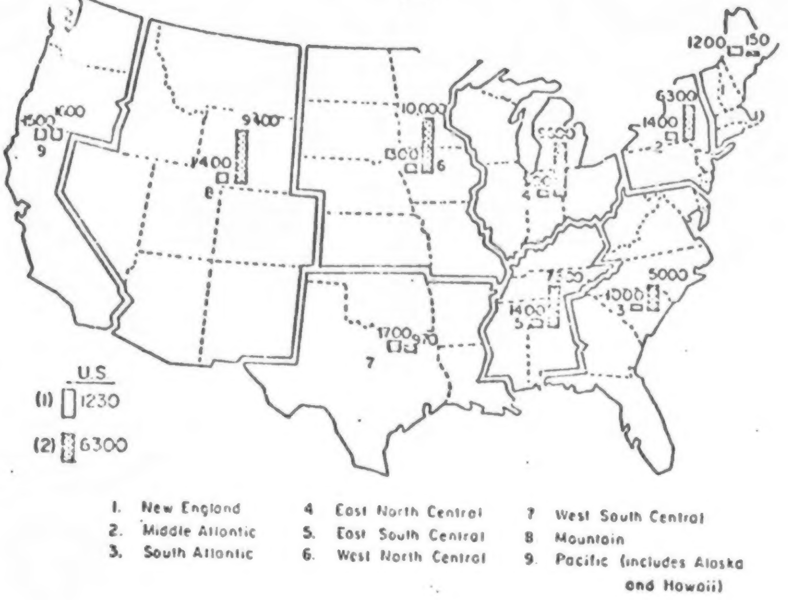
1200
150
6300
1400
2
1
10,000
1300
6
9400
1400
8
1500
1600
9
7550
1400
5
5000
1000
3
1700
970
7
4
U.S.
(1) 1230
(2) 6300
1. New England
2. Middle Atlantic
3. South Atlantic
4. East North Central
5. East South Central
6. West North Central
7. West South Central
8. Mountain
9. Pacific (includes Alaska and Hawaii)

FIGURE C-1. AVERAGE VOLUME IN TONS PER YEAR OF (1) ALUMINUM SCRAP PROCESSORS, AND (2) ALUMINUM SCRAP CONSUMERS, BY REGION, 1969

Source: Extensive Survey

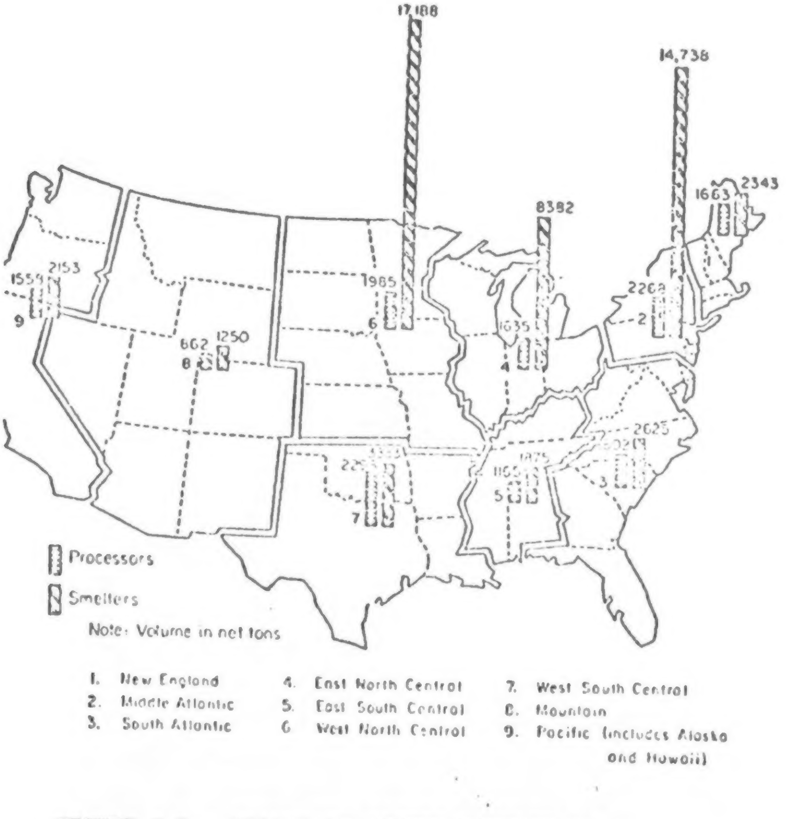
17,188
14,738
8382
1663
2343
1985
6
2268
2
1555
2153
9
662
1250
8
1635
4
2025
1875
1165
5
3
7
Processors
Smelters
Note: Volume in net tons
1. New England
2. Middle Atlantic
3. South Atlantic
4. East North Central
5. East South Central
6. West North Central
7. West South Central
8. Mountain
9. Pacific (includes Alaska and Hawaii)

FIGURE C-2. VOLUME OF COPPER HANDLED BY TYPE OF RECYCLE BY REGION

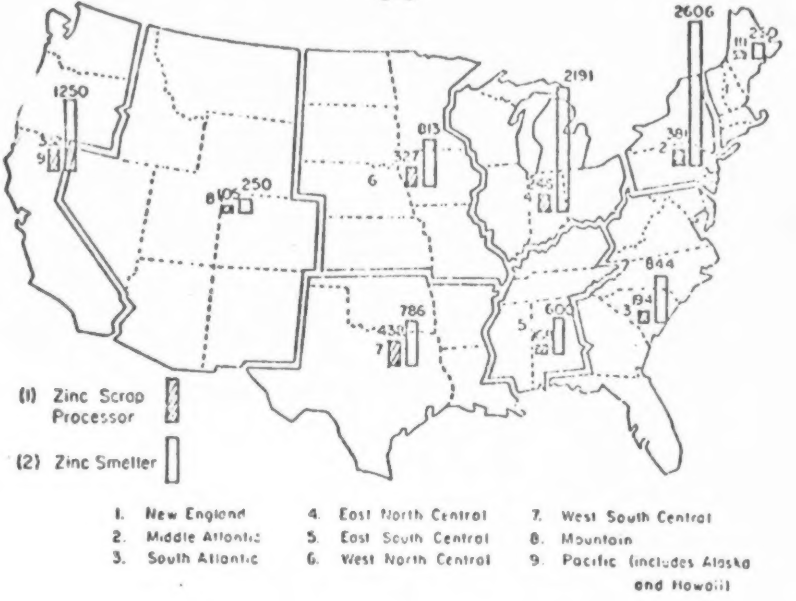
2606
111
232
1250
2191
813
327
6
381
2
9
250
105
8
245
4
844
786
430
7
600
5
194
3
(1) Zinc Scrap Processor
(2) Zinc Smelter
1. New England
2. Middle Atlantic
3. South Atlantic
4. East North Central
5. East South Central
6. West North Central
7. West South Central
8. Mountain
9. Pacific (includes Alaska and Hawaii)

FIGURE C-3. AVERAGE SIZE IN TONS PER YEAR OF ZINC OF (1) ZINC SCRAP PROCESSORS AND (22) ZINC SMELTERS, BY REGION, 1969
Source: Extensive Survey

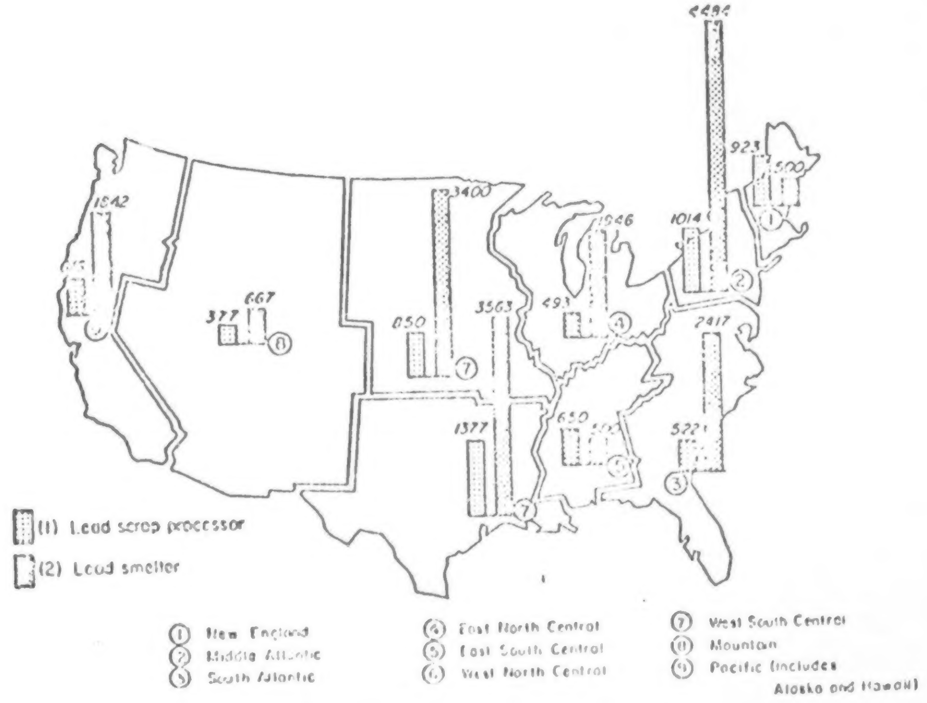
923
500
1842
3400
1946
1014
667
377
850
3563
493
2417
1377
650
522
(1) Lead scrap processor
(2) Lead smelter
① New England
② Middle Atlantic
③ South Atlantic
④ East North Central
⑤ East South Central
⑥ West North Central
⑦ West South Central
⑧ Mountain
⑨ Pacific (includes Alaska and Hawaii)

FIGURE C-4. AVERAGE SIZE IN TONS PER YEAR OF LEAD OF (1) LEAD SCRAP PROCESSORS, AND (2) LEAD SMELTERS, BY REGION, 1969
Source: Extensive Survey

In scrap pretreatment, the scrap is treated by a number of processes to densify it and/or to separate the nonferrous metal from gross impurities to render the scrap more amenable to smelting. Smelting is an operation whereby the scrap is partially purified by heat. From the smelting operation, the scrap is given a final purification in the refining operation and finally cast into the desired form.

Processes

Processes comprise specific arrangements of equipment that accomplish chemical or physical transformation of the scrap materials into end products, intermediate products, and waste materials. Other process outputs include waste streams to the air, water, and land. When two or more different combinations of process steps accomplish the same chemical or physical transformation but have different environmental impact, each combination is a distinct process. An example of a process is Fire/Refining in the Copper Industry. Black copper and/or blister copper are treated in the molten state to remove residual metal values and produce a fire-refined copper melt. Other process outputs include atmospheric emissions, liquid wastes, and solid wastes.

Process Steps

Process steps are the basic components of a process that utilize process equipment or materials handling equipment, not including control equipment. In each case where a piece of process equipment has two or more cycles or phases with distinctly different emissions to the atmosphere, such cycles can be considered sequential process steps. An example of a process step is blowing the melt with air in the fire-refining process.

Future Trends

Modern technology, environmental effects, and the shift in the flow of raw materials are all having a direct impact on the secondary nonferrous metals industry. For example, the characterization of the raw materials is changing. Low-grade scrap which at one time was disposed of by landfill is now being recycled to the secondary industry. Large volumes of metal-laden dust are no longer emitted to the atmosphere but are collected in dust control equipment. The collected dust becomes a source of raw material to the secondary industry.

ENVIRONMENTAL IMPACTS

Atmospheric Emissions

The secondary nonferrous metals industry is one of the sources of environmental pollution. The pollution may be in the form of atmospheric emissions, liquid wastes, and solid wastes. Atmospheric emissions generally contain particulate and gaseous materials, both of which are sources of pollution and potential health hazards.

The composition of the atmospheric emissions depends on the segment of the industry from which the emissions are derived. However, it has been established that the industry as a whole emits such metallic materials as lead, zinc, mercury, arsenic, cadmium, antimony, precious metals, magnesium, nickel, copper, manganese, and aluminum.

Emissions factors for atmospheric emissions for every segment of the industry are not available although it can be said that, in many cases, significant quantities are emitted. For example, the raw emissions factor for metallic zinc sweating process with zinc chloride was reported to be 10.8 lb of particulates/ton of scrap, whereas the raw emission factor for sweating residual scrap was reported at 24.5 lb/ton of scrap processed.

Morphology of the particles is dependent on the type of scrap, segment from which the particulates are generated, and many other factors. In most cases, the particulates' sizes range from less than 0.1 micron to several microns. Particle shape will vary from spherical to irregular shapes.

Gaseous emissions also depend on the segment of the industry and the processing step. In general, atmospheric emissions may contain, in addition to the combustion products, harmful materials like sulfur oxides, halides, inorganic acids, hydrocarbons, and ammonia.

A substantial portion of the pollution from the industry comes from the burning of fuels to provide energy for the processes. Quantitatively, data are not available on the energy demand for this energy. However, the primary sources of energy for the secondary nonferrous metals industry are: (1) natural gas, (2) fuel oil, (3) coke, and (4) electricity. Data on quantities of energy consumed by this industry are not readily available.

Emission of Liquid Wastes

The secondary nonferrous metals industry can be a significant source of liquid wastes as water is used for many applications throughout the industry. For example, in the aluminum segment, aqueous wastes are generated principally in these operations: cooling molten aluminum alloy, wet scrubbing of fumes during chemical magnesium removal, and the wet milling of aluminum melt residues such as dross and slag. Ingots and shot are cooled with water by direct contact with the mold and metal. Magnesium content in aluminum alloys is adjusted by the chemical removal of magnesium using either chlorine or aluminum fluoride. Wastewaters containing very large levels of suspended and dissolved solids are produced during the wet milling of residues containing aluminum.

Another example is the copper segment, where wastewater is generated in 15 of 25 processes.

Composition of these aqueous wastes depends on the segment of the industry generating the wastes. Some of the wastes are simply cooling water and can be recycled with a minimum of treatment. Other wastes contain a wide variety of soluble and insoluble metallic and nonmetallic materials. An example of the contaminants in the aqueous wastes for the secondary aluminum industry is shown as follows.

Composition of Aqueous Waste From Aluminum Segment

- Sulfate
- Chloride
- Fluoride
- Aluminum
- Calcium
- Copper
- Magnesium
- Nickel
- Sodium
- Zinc
- Cadmium
- Lead
- Manganese
- Oil
- Grease
- Phenols

Also, metal values such as arsenic, mercury, and barium are found in the aqueous wastes. While many of these heavy metal values may be harmless, metals such as cadmium, mercury, and arsenic are known to be toxic.

In summary, the secondary nonferrous metals industry is a potential source of aqueous wastes to the environment. If these wastes are not controlled by treatment before discharging or if they are not recycled, serious pollution problems could arise.

Solid Waste Emissions

Solid wastes are generated in this industry by the nature of the numerous processes. Slag from the smelting of copper and drosses from the aluminum industry are examples. Drosses from the treatment of aqueous wastes generated in the production of electrolytic copper is another example. Another source of solid wastes common to this and other industries is the dust collected in control equipment such as baghouses. Solid wastes such as slurries (mixtures of solids and liquids) and fine particulate materials are disposed of in lagoons, in landfills, or, in many cases, become a source of raw material for the secondary industry.

As with the other wastes from this industry, the composition of this waste is dependent on the process and processing steps in each segment. These wastes are known to contain metallic and nonmetallic materials found also in atmospheric emissions, aqueous wastes, and the raw materials to this industry. Many of them are toxic.

In summary, this industry generates substantial quantities of solid wastes. In many cases, serious pollution problems can result if these wastes are not disposed of in a safe and adequate manner.

RAW MATERIALS

Raw materials for the industry are divided into three broad categories as follows.

(1) Old Scrap. This is the kind most commonly associated with the scrap business though not necessarily the largest in volume. Old scrap is discarded, dismantled, worn out metallic elements. Typical examples are: a radiator removed from a wrecked car; copper pipes taken from an old building; high strength, heat resistant rotor blades once used in a jet engine, applicances discarded by homeowners.

(2) New Scrap. This is metal which has never been made into or used as an end product. It comes from industrial sources and is the by-product of some part of the manufacturing process. Common examples include: a manufacturer of aluminum cans buys huge coils of sheet aluminum and when the can lids (tops) are made on stamping (blanking) machines which punch the lids out of sheets of original material, the remaining skeleton is scrapped and usually described as clippings; or, when household faucets are produced in foundries which make the body of the faucet in a sand mold to produce a casting; or, when pouring molten

metal into the mold some will spill over the mold opening or into the sand rather than into the mold cavity and these spillings are scrapped because they pick up impurities or become mixed with dirt and sand. These are usually called foundry spillings or residues.

This "new" scrap differs from "old" scrap in that it is generally available in larger and more uniform lots; and its metallic constituents are more readily identifiable.

(c) Obsolete Scrap. This category consists of generally new, unused but technologically obsolete parts, over-runs from the production process, inventory that is no longer required, repossessed merchandise or auctioned material. Some examples: The U. S. Government sells for scrap, spare parts for a radar network which is no longer needed for national security; or a railroad has in stock a type of journal bearing but decides to standardize its entire fleet of cars with foller bearings, making the solid bearings available as scrap.

A detailed description of the source of raw materials for each segment is included in the descriptions which follow.

PRODUCTS

Products from the Secondary Industry are generally ingots of refined or partially refined metals which are shipped to the fabricator for processing into a finished product or shipped to the Primary Industry for further refining. In some cases, the product is consumed as produced from the process as described in discussions which follow on the products from each industry segment.

PROCESS DESCRIPTION OF ALUMINUM SEGMENT OF SECONDARY NONFERROUS METALS INDUSTRY

Tonnage-wise, the aluminum segment constitutes the second largest segment of the secondary nonferrous metals industry. Based on 1969 data, U. S. production rate was 1,056,000 tons. Emissions from this segment include fine particulate matter and gaseous materials which may become atmospheric pollutants, and aqueous and solid wastes which, if not properly disposed of, will pollute the water system and the land.

Raw Materials

Sources of raw materials to this segment include both new and old scrap. The new scrap, that which comes from a fabricator who does not choose or is not equipped to recycle the scrap, accounts for about 75 percent of the scrap. Old scrap, a product of obsolescence, becomes available to this segment when consumer products have reached the end of their economic life and have been discarded, and accounts for approximately 25 percent of the domestic scrap consumed in the U. S. Basically, the scrap can be divided into 6 categories: (1) sheet and castings, (2) new clippings, (3) borings and turnings, (4) high aluminum-iron alloy scrap, (5) drosses or skimmings with fluxing salts, and (6) drosses or skimmings without fluxing salts.

The choice of scrap which a secondary smelter purchases for use in its furnaces is determined by the equipment or flowsheet of the individual smelter. Obviously, a smelter with no burning or drying equipment for processing oily borings and turnings cannot use this material. Likewise, smelters without crushing or residue processing equipment are similarly restricted in the types of scrap they can process. Air pollution codes in many cities also have limited the processing of heavily painted material such as painted siding or venetian blinds. Hence, smelters having limited processing equipment must be selective in scrap purchasing, while more sophisticated smelters have greater latitude in scrap purchasing.

Products

The products from the secondary aluminum segment are: (1) aluminum alloy castings, (2) aluminum shot, (3) hot metal, (4) aluminum fines, and (4) hardeners. The aluminum alloy castings may be in the form of ingots (15 to 30 lb), billets (approximately 1000 lb), notched bar (2 to 5 lb), and hardeners of different weights. "Hot metal" is molten aluminum alloy which is tapped directly from the furnaces into preheated crucibles with capacities up to 15,000 lb and transported directly up to distances of 300-400 miles to the consumer (foundries). Aluminum shot is small beads of quenched aluminum metal. Aluminum fines are the undersize (-20 microns) material from screening of the aluminum scrap treated by the burning/drying process.

Process Description

The recovery of aluminum from scrap normally involves two manufacturing operations: (1) scrap pretreatment, and (2) smelting-refining. The two manufacturing operations and the individual processes under each operation are shown in the attached industry segment flowsheet entitled "Aluminum Segment of the Secondary Nonferrous Metals Industry".

Scrap Pretreatment

Aluminum scrap is pretreated prior to smelting to remove contaminants and physically prepare the material for further processing. Three types of pretreating (mechanical, pyrometallurgical, and hydrometallurgical) are used. The pretreatment process employed depends on the type of scrap. The individual pretreatment processes are indicated in the flowsheet by numbers 1 through 6.

Shredding/Classifying Process (1). The iron core and neoprene or plastic insulation is removed from electrical conductor scrap containing superpure aluminum by the Shredding/Classifying Process (1). This treated aluminum scrap is used to produce, among other things, hardeners. The processing steps are: (a) shredding of the scrap into small pieces to separate the iron core and plastic coating from the aluminum alloy, (b) magnetically treating to remove the ferrous portion of the scrap, and (c) separating the neoprene or plastic insulation from the high-purity aluminum by an air classification system.

Energy demand for this process is that necessary to drive the equipment.

The Shredding/Classifying Process (1) is a minor source of atmospheric emissions. However, significant quantities of solid wastes--ferrous scrap and neoprene or plastic waste--are generated. The scrap is recycled and plastic waste is disposed of in a landfill.

This process has no serious potential pollution problems of any kind.

Baling Process (2). Densification or compaction of sheet, castings, and clippings is achieved by baling in specially designed baling machines. Baling is normally conducted by the scrap dealer or at the source of scrap generation. Occasionally, the baled scrap is further processed by crushing and screening prior to smelting.

Energy demand is limited to that needed to drive the equipment.

Atmospheric emissions from this process are composed of suspended particulate matter containing primarily dirt from the scrap and alumina resulting from the oxidation of the aluminum dust. Solid wastes generated are scrap iron, magnesium, and other scrap found mixed with the scrap aluminum.

The quantity of pollutants generated by baling is low; therefore, the process has a low pollution potential.

Crushing/Screening Process (3). Borings and turnings which result from machining and drilling are treated by the crushing/screening process to densify the aluminum values and remove contaminants. This process entails three process steps: (a) crushing in a hammermill to densify the scrap, (b) deoil, (c) dry, (d) screening to remove aluminum fines, and then (e) passing over a magnetic separator to remove the tramp iron.

Energy demand for this process is that needed to drive the equipment and oil/gas for the dryer.

The process produces essentially no atmospheric emissions and no aqueous wastes. The quantity of solid wastes such as tramp iron generated is expected to be low as the majority of the iron is removed prior to crushing.

The process has no potential for serious pollution problems.

Burning/Drying Process (4). Borings, turnings, and other organic-contaminated scrap are, in some cases, smelted without removal of the organic contaminants and water. However, the scrap is generally treated to remove the water and organic matter such as machining oils by the burning/drying process. This process involves several processing steps: (a) crushing in a hammermill to densify the scrap, (b) heating the crushed material in a gas-oil fired rotary dryer to remove organic contaminants and water, (c) screening the dryed material to remove the aluminum fines which are sold for explosive or pyrotechnic purposes, and (d) magnetically treating the remainder to remove the tramp iron.

Energy demands for this process are: (a) gas or oil to supply the heat to burn the organic compounds and evaporate water from the scrap, and (b) that required to drive the equipment.

The burning/drying process is a source of atmospheric emissions and solid wastes. The atmospheric emissions consist of gaseous products primarily carbon dioxide from combustion of the fuels and the organic contaminants, and particulate matter entrained in the gases. The gases may also contain some chlorides, possibly fluorides and sulfur oxides, depending on the composition of the organic contaminants. The particulate matter is parimarily alumina resulting from oxidation of the small particulates of aluminum swept from the kiln by the combustion gases. The solid waste is primarily tramp iron removed in the magnetic treatment of the crushed scrap.

Thus, the burning/drying process presents serious potential pollution problems if the emissions are not controlled properly, especially in those cases where the organic contaminants contain significant quantities of halides, where significant quantities of alumina are emitted, and where oil is used in place of gas as the fuel. Normally, the atmospheric effluent from the Burning/Drying Process is treated with an afterburner located in the stack. However, wet scrubbers are beginning to replace the afterburner, in which case the air pollution problem can become a water pollution problem. The solid wastes generated are not a serious pollution problem.

Sweating Process (5). The contaminant-iron is removed from high iron scrap by the sweating process, employing a sloping hearth or grate-type furnace. The processing steps employed are: (a) heating the scrap to melt the aluminum and other low melting constituents which flow by gravity into a collecting pot or ingot mold, and (b) casting the melt into pigs (30 lb ingots) or sows (up to 1000 lb ingots) in air-cooled molds. The furnace is heated to approximately 1400 F to separate the low melting aluminum along with other low melting materials from the scrap.

Energy demand for this process is natural gas and that needed to drive the equipment.

Emissions from this process are: (a) atmospheric emissions composed of the combustion products and particulate matter, primarily aluminum trioxide, and (b) solid wastes containing iron contaminated with aluminum and other nonferrous elements such as zinc, magnesium, and lead. Gaseous emissions from the furnace are generally passed through an afterburner before being emitted to the atmosphere. The solid wastes are discarded.

The process can cause serious atmospheric pollution problems, if not properly controlled. According to a survey(1), raw (uncontrolled) particulate emission factor from the sweating process is reported to be 14.5 lb/ton (7.25 Kg/MT) of metal processed. This factor does not include gaseous emissions. Composition of the emissions, both gases and particulate matter, will need to be determined by source testing. A baghouse is usually used to control dust emissions.

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(1) Duprey, R. L., "Compilation of Air Pollution Emission Factors", U. S. Dept. HEW, NAPCA, Raleigh, North Carolina, pp 28-29 (1968).

The solid wastes should cause no pollution problems.

Leaching Process (6). Leaching removes the contaminants such as fluxing salts and other water soluble components from drosses, skimmings, and slags to produce an aluminum scrap suitable for the smelter. The processing steps are: (a) wet milling of the scrap in an attrition mill or a ball mill to densify the scrap, (b) screening to remove the fines and dissolved salts, (c) drying to remove the water, and finally (d) treating with a magnetic separator to remove the ferrous portion.

Energy required is that needed to operate the equipment and to dry the crushed scrap.

The process produces no atmospheric emissions except possibly in the drying step. However, significant quantities of water and solid wastes are produced. The water wastes containing dissolved and suspended solids are disposed of via a series of settling ponds. The solid wastes result from the settling pond and the undersize material from the screening operation.

The process does not present an atmospheric pollution problem; however, there is a water pollution problem as well as a problem relating to disposal of the solid wastes. From a recent survey of the secondary aluminum industry by Battelle, the water pollution problem essentially can be handled by disposing of the water wastes in settling ponds. The solid wastes can be placed in a landfill.

Smelting/Refining Operation

Reverberatory (Chlorine) Smelting-Refining Process (7). Alloy ingots, shot, and hot metal are produced from treated aluminum scrap, sweated pigs, and, in some cases, untreated scrap by this process.

The process steps are: (a) charging of the scrap to the furnace; (b) melting of the scrap; (c) fluxing to remove certain contaminants; (d) alloying, i.e., the addition of certain metals to produce a melt of the desired composition; (e) mixing of the melt to produce a homogeneous material; (f) demagging with gaseous chlorine; (g) degassing with an inert gas such as nitrogen or nitrogen-chlorine mixture to remove entrapped hydrogen and other gases; and (h) skimming to remove the slag or dross containing the impurities. After slag removal, the melt is (1) poured into molds and cast into alloy ingots, billets, and notched bars; or (2) poured onto a vibrating feeder and quenched in water to produce shot; or (3) poured into heated crucibles and transported to the consumer as "hot metal", i.e., molten metal. Any given smelter may not incorporate all of these steps into the process, but may use a combination of the steps.

The reverberatory furnace, a rectangular box usually ranging in capacity from 15 to 90 tons is used in this process to smelt and refine the aluminum. The furnace is direct fired; furnace fuel may be either natural gas or fuel oil. Heat input ranges from 2,000 to 2,500 Btu per pound of alloy. Additional energy is required to operate the auxiliary equipment.

Emissions from this process are atmospheric emissions (gases and particulate matter), aqueous wastes, and solid wastes. In addition to the combustion products, the gases may contain chlorine, hydrogen chloride, zinc chloride, magnesium chloride, aluminum chloride, and aluminum oxide, along with minute quantities of a wide variety of other metals contained in the scrap and added during the smelting-refining. Likewise, the aqueous and solid wastes contain a wide variety of metal values depending on the scrap.

All processing steps are sources of atmospheric emissions. The addition of scrap to the furnace and melting of the scrap is a major source of atmospheric emissions depending on the quality of the scrap. Quantitative data are not available for the secondary aluminum segment. However, for the brass and bronze segment,(2) raw emission

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(2) "Air Pollution Aspects of Brass and Bronze Smelting and Refining Industry", U. S. Dept. HEW, NAPCA, Raleigh, North Carolina (1969).

factors for the charging step are reported to range from 11.7 to 59.0 lb of particulate matter per ton of feed. Comparable emission factors may be expected for the charging step for the secondary aluminum segment, especially at those smelters charging untreated scrap and scrap containing significant quantity of volatile impurities such as zinc.

Fluxing is practiced to some extent at most secondary aluminum smelters. Some of the components volatize during the smelting-refining while others, along with impurities or contaminants in the scrap aluminum, are entrained in the furnace exit gases. Composition of the atmospheric emissions will vary depending on the scrap and the flux. However, these emissions have been found to contain such elements as sodium, aluminum, magnesium, calcium, iron, lead, manganese, potassium, chromium, zinc, and nickel, in addition to the combustion gases and hydrogen halides.

Alloying produces minor amounts of fumes and dust which are carried from the furnace by entrainment in the combustion gases and other gases formed during this processing step.

Mixing of the melt to insure uniform composition and to mix the fluxes into the melt is generally accomplished by injecting nitrogen gas below the surface of the melt. As a result, mixing becomes a significant source of atmospheric emissions. The gaseous portion of the emissions is composed of nitrogen, hydrogen halides, and other volatile components. Composition of the particulate matter is similar to the emissions from the fluxing processing step.

Removal of magnesium (demagging) is accomplished by chlorination. This entails lancing the molten aluminum with chlorine gas which reacts with the aluminum to form aluminum chloride. The aluminum chloride then reacts with the magnesium to form magnesium chloride which is carried along with other metallic and nonmetallic impurities and gaseous contaminants to the surface of the melt. Some of these are trapped in the flux on the surface of the melt, while the remainder is volatized and becomes part of the atmospheric emissions.

The demagging step is a major source of atmospheric emissions in the secondary aluminum segment. Raw emission factor for this processing step is reported(3) to be 1000 lb of particulate matter per ton of chlorine used (500 Kg/t).* Through the use of a baghouse as the control device (which does not remove the gases), the particulate emissions factor is reduced to 50 lb of particulate matter per ton of chlorine used (25 Kg/t).

In order to remove the gases and the particulate matter, a wet scrubber using a 10 percent caustic solution as the scrubbing medium in series with a baghouse is employed. In one installation,(4) two of the scrubbers were arranged in parallel. After scrubbing, the fumes were sent to a five-compartment baghouse for particulate removal. In this installation, the scrubber removed virtually all of the hydrogen chloride gas and greater than 90 percent of the chlorine gas. Wet scrubbing also hydrolyzes and removes the majority of the chlorides such as aluminum chloride as the corresponding oxides or hydroxides.

Composition of the atmospheric emissions from the demagging step depends somewhat on the composition of melt and fluxes employed in the fluxing step. However, in addition to the combustion gases, the gaseous portion of the atmospheric emissions is composed of chlorine, hydrogen halides such as hydrogen chloride, along with chlorides of the volatile metals. The particulate emissions are composed of such metal values as calcium, copper, magnesium, nickel, zinc, cadmium, and aluminum.

Degassing of the molten aluminum prior to casting is necessary to remove hydrogen absorbed from the atmosphere or other sources of moisture or water vapor. The metal is degasified by lancing with dry nitrogen, chlorine, or mixtures of the two gases. If a smelter does not have adequate ventilation and air pollution abatement equipment, nitrogen is used for degassing, because degassing with chlorine or mixtures of chlorine and nitrogen results in severe fuming. Composition of these fumes may vary from smelter to smelter, but, in general, is similar to those emissions from the demagging processing step.

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(3) Duprey, F. L., "Compilation of Air Pollution Emission Factors", U. S. Dept. HEW, NAPCA, Raleigh, North Carolina, pp 28-29 (1968).

(4) Danielson, John A., ed., Air Pollution Engineering Manual, U. S. Dept. HEW, Cincinnati, Ohio, pp 284-292 (1967).

* Kg/t = kilograms per ton (1000 Kg).

Skimming to remove the dross or slag collected on the surface of the melt and casting of the ingots are minor sources of atmospheric emissions.

Another potential source of atmospheric emissions results from cooling and from storage of the slag (drosses and skimmings) while enroute to the processor. If allowed to come in contact with water, the nitrides and carbides of aluminum react with the water to form hydrocarbons and ammonia which are liberted to the atmosphere.

Aqueous wastes are generated during ingot and shot cooling or quenching, and from scrubbing of the emissions from the reverberatory furnace. Also, if the drosses and skimmings are stored in the open, runoff water may become a source of aqueous wastes. The waste cooling water is disposed of by vaporization, discharging directly to a municipal sanitary sewer or stream, or a pond. In a survey of 50 secondary aluminum plants, 24 discharged to sewers or streams, 4 discharged to a pond, 13 recycled continuously, 7 discharged after recycle, and 2 vaporized the water. This wastewater contains significant quantities of heavy metals, phenol, and other contaminants and is, therefore, a potential source of water pollution.

The other source of wastewater from the Reverberatory (Chlorine) Smelting-Refining Process (7) is that from the wet scrubbers. This waste which may or may not be neutralized is discharged to ponds. That which has not been neutralized has a pH of about 1.5 and contains hydrolyzed metal chlorides of aluminum, magnesium, zinc, manganese, cadmium, copper, nickel, and lead. The neutralized scrubbing liquor with a pH of 9 to 11 contains sodium, potassium, and calcium and lesser quantities of the heavy metals, aluminum and magnesium.

Solid wastes generated by this process include: (1) drosses and skimmings from the process itself, and (2) wastes from the air pollution control equipment. The drosses and skimmings are recycled, while the others are probably disposed of by routine methods such as landfill. If not properly prepared, the leachate from the landfill can enter the ground water and cause pollution problems.

Thus, the Reverberatory (Chlorine) Smelting-Refining Process (7) is a major source of atmospheric emissions from the aluminum segment of the secondary metals industry. These emissions containing gaseous and fine particulate matter present serious pollution problems if emitted to the atmosphere. Raw emission factors exclusive of the demagging processing step for this process have been reported to be 4.3 lb of particulate matter per ton (2.15 Kg/t of metal processed. Using a baghouse or an electrostatic precipitator as the pollution control device reduced the emission factor to 1.3 lb of particulate matter per ton (0.65 Kg/t of metal processed. Raw emission factor for the demagging processing is reported at 1000 lb of particulate matter per ton of chlorine (500 Kg/t) used. The emission factor is reduced to 50 lb of particulate matter per ton of chlorine (25 Kg/MT) used(3) by employing a baghouse as the control device.

Currently, most of the secondary smelters using chlorine in the demagging processing step employ wet scrubbers alone or in combination with baghouses to reduce the atmospheric emissions. Although emission factor data are not available, it is expected that this combination of pollution abatement equipment will remove the gaseous emissions such as chlorine and hydrogen chloride as well as the particular matter more efficiently than either the baghouse or electrostatic precipitator. In one installation, the scrubber removed virtually all of the hydrogen chloride gas, greater than 90 percent of the chlorine, and greater than 80 percent of the aluminum chloride.

Particle morphology of the particulate emissions, i.e., particle size and shape, is somewhat dependent upon the composition of the scrap and the processing parameters. However, in general, the particulate matter is composed of particles ranging in size from a few hundredths of a micron (approximately 0.05 micron) to several microns (approximately 2 to 5 microns). In one case, the fume from salt-cryolite mixtures was found to be composed of particles ranging in size from less than 2 microns to less than 0.1 micron. In another case the fume from a demagging operation was found to be composed of a mixture of particles with 90 to 95 percent less than 1 micron in diameter. This small particle size makes it difficult to collect the emissions in baghouses and electrostatic precipitators.

The emissions are generally composed of particles exhibiting both regular and irregular particle morphology. The morphology will range from acicular shapes (long needle shape particles) to spherical particles.

Solid wastes and aqueous wastes, if not disposed of properly, can present pollution problems.

Reverberatory (Fluoride) Smelting-Refining Process (8). This process is essentially the same (i.e., the same processing steps are employed as in Reverberatory (Chlorine) Smelting-Refining) except that aluminum fluoride (AlF_3) is used in place of gaseous chlorine in the demagging processing step. In Process 8, the magnesium is removed by mixing solid AlF_3 into the molten metal. The AlF_3 reacts with the magnesium to give aluminum metal and magnesium fluoride which floats or is carried by the mixing gas to the surface of the molten metal and is removed as part of the dross or skimmings.

Conducting the demagging with AlF_3 results in a significant reduction in the quantity of atmospheric emissions. Consequently, the problems associated with atmospheric pollution are significantly reduced, yet not completely eliminated as significant quantities of atmospheric pollutants are discharged. Instead of large quantities of chlorine gas, the emissions contain fluorides as gaseous fluorides or fluoride dusts. If not properly controlled, the fluorides as well as the other particulate matter and gases in the effluent can cause serious pollution problems. The atmospheric emissions may be controlled by the same dry or wet methods used in Process 7.

Aqueous waste generated in this process consists of waste cooling water generated during ingot and shot formation. This waste water is disposed of either by discharging to sewers, streams, or ponds; recycled continuously; recycled partially; or evaporated (see discussion of waste cooling water under Process 7 as same treatment and disposal methods are employed). The wastewater from the fume scrubber (which is recycled) is first treated with caustic to remove the fluoride. The solids formed during neutralization are separated in settling tanks and the effluent is recycled to the scrubber system.

Solid wastes generated by this process are: (1) drosses and skimmings from the process itself, and (2) solids from the air pollution control equipment. The dross and skimmings are recycled. Solid waste (sludge) from the wet scrubber is dewatered and placed in a landfill. If not properly prepared, the leachate from the landfill can enter the underground water system and cause pollution problems. Those smelters using the dry collection system also dispose of the fume dust and bag coating substances in landfills. Although the fluorides are considered to be insoluble, the solubility may be great enough to contaminate ground water.

Because of the toxic and hazardous nature of the pollutants generated by this process, the process presents serious pollution problems if these pollutants are not collected and disposed of in a proper manner.

Crucible Smelting-Refining Process (9). For producing small quantities of aluminum alloy castings, i.e., up to approximately 1000 lb, the Crucible Smelting-Refining Process (9) is used. The processing steps are: (a) charging of the melt to the furnace, (b) melting of the charge, (c) fluxing to remove the contaminants if necessary, (d) alloying to produce a melt of the desired composition, (e) mixing to homogenize the molten metal, (f) demagging, (g) degassing, and (h) skimming. Afterwards, the melt is poured and cast into the desired shapes. Any given smelter may not incorporate all of these steps into the process, but may use a combination of the steps depending on the source of scrap.

Energy demand is limited to that required to operate the equipment and to heat the furnace. The furnace is heated indirectly with gas or fuel oil as the source of fuel. However, electricity may also be used as the source of energy.

Potential environmental pollutants from this process are: atmospheric emissions which are composed of gases and particulate matter, aqueous wastes containing dissolved and suspended solids and solid wastes. Since this process is quite similar to reverberatory smelting-refining except for the size of operation, see discussions in the previous sections on Processes 7 and 8 for data on composition of pollutants, processing steps generating the wastes, and disposal of the pollutants.

This process has the potential for generating significant pollution problems.

Induction Smelting-Refining (10). This process produces hardeners, alloys of known composition, which are used to introduce precise amounts of particular metals into a melt to meet predetermined specifications. The most common hardening agents are titanium, boron, and chromium. The hardeners are produced by melting and blending electrical conductor scrap (superpure aluminum) with the hardening agent in an induction furnace. The processing steps are: (a) charging of the scrap to the furnace, (b) melting of the scrap, (c) blending the molten metal with the alloying agent, (d) skimming of the melt to remove the oxides on the surface, (e) pouring of the melt, and (f) casting into notched bars.

Energy demand is limited to that needed to run the equipment and the electricity to melt the scrap.

The process produces small quantities of atmospheric emissions and aqueous and solid wastes. The atmospheric emissions contain, in addition to aluminum, small amounts of the alloying agent and other metals found in the scrap. These emissions are generated in all of the processing steps. The aqueous wastes are generated during the casting of the notched bars, whereas the solid wastes are drosses (skimmings from the surface of the melt). These wastes can be collected and disposed of by the methods employed in Process 7.

This process has a low potential for the production pollutants.

Rotary Furnace Smelting-Refining (11). This process is employed to recover the aluminum values from such raw materials as drosses to produce high aluminum ingots which are refined in the reverberatory furnace. The processing steps are: (a) charging of the scrap and flux, (b) melting of the charge, (c) pouring, and (d) casting of the ingots.

The energy demand for this process is that needed to drive the equipment and natural gas or fuel oil to heat and melt the charge.

The process produces atmospheric emissions composed of gases such as the combustion products, entrained air, and volatile metal values and particulate matter such as the flux and particles of the charge. Solid wastes are the slag containing impurities extracted from the aluminum and the sludge from the wet scrubber. Aqueous waste consists of primarily the cooling water used in casting the ingots. These wastes may be disposed of by methods used for disposal of similar wastes from other processes.

The process can cause serious pollution problems, if not properly controlled.

Population of Secondary Aluminum Processors

(1) Alloys and Chemicals Corporation
4365 Bradley Road SW
Cleveland, Ohio 44109
Telephone: (216) 661-8600

(2) Aluminum Billets, Inc.
3786 Oakwood Avenue
Youngstown, Ohio
Telephone: 792-6511

(3) Aluminum & Magnesium
Incorporated
Huron and W. Monroe Streets
Sandusky, Ohio

(4) Aluminum Smelters Incorporated
322 Legion Avenue
New Allen, Connecticut

(5) Aluminum Smelting and Refining
Company, Inc.
5463 Dunham Road
Maple Heights, Ohio 44137
Telephone: 662-3100

(6) Apex Smelting Company
Division of Amax Aluminum Company
2515 West Taylor Street
Chicago, Illinois
Telephone: (312) 332-2214

(7) Aurora Refining Company
Box 88
Aurora, Illinois

(8) Barnum Smelting Company
Barnum Avenue
Bridgeport, Connecticut 06608

(9) Batchelder-Blasius, Inc.
Post Office Box 5503
Spartanburg, South Carolina 29301

(10) Bay Billets Inc.
1364 Olds Street
Sandusky, Ohio

(11) Joseph Behr and Sons, Inc.
1100 Seminary Street
Rockford, Illinois
Telephone: (815) 962-7721

(12) Belmont Smelting & Refining
Works, Inc.
320 Belmont Avenue
Brooklyn, New York 11207
Telephone: DI2-4900

(13) W. J. Bullock, Inc.
Post Office Box 539
Fairfield, Alabama 35064

(14) Colonial Metals Company
Columbia, Pennsylvania
Telephone: (717) 684-2311

(15) J. R. Elkins, Inc.
518 Gardner Avenue
Brooklyn, New York 11222

(16) Excel Smelting Corporation
1300 North Seventh Street
Memphis, Tennessee 38107

(17) Federated Metals
Division of American Smelting
and Refining Company
12 Pine Street
New York, New York

(18) Firth Sterling, Inc.
3113 Forbes Avenue
Pittsburgh, Pennsylvania
15230

(19) General Smelting Company
Division of Wabash Smelting
Incorporated
2901 EW Moreland Street
Philadelphia, Pennsylvania
Telephone: GA3-3200

(20) Gettysburg Foundries
Post Office Box 421
Gettysburg, Pennsylvania
17325
Telephone: 334-5616

(21) Hall Aluminum Company
1751 State Street
Chicago Heights, Illinois

(22) Harco Aluminum, Inc.
4528 West
Chicago, Illinois 60651

(23) Henning Brothers & Smith, Inc.
91-115 Scott Avenue
Brooklyn, New York

(24) Holtzman Metal Company
5223 McKissock Avenue
St. Louis, Missouri 63147

(25) North American Smelting Company
Post Office Box 1952
Marine Terminal
Wilmington, Delaware
Telephone: OL4-9901

(26) Northwestern Metal Company
North 27th Street
Lincoln, Nebraska

(27) Paragon Smelting Corporation
36-08 Review Avenue
Long Island City, New York 11101
Telephone: (212) RA9-3641

(28) Pioneer Aluminum, Incorporated
3800 East 26th Street
Los Angeles, California

(29) George Sall Metals Company, Inc.
2255 East Butler Street
Philadelphia, Pennsylvania 19137
Telephone: (215) PI3-3900

(30) Silberline Manufacturing Company, Inc.
Lansford, Pennsylvania
Telephone: (717) 645-3161

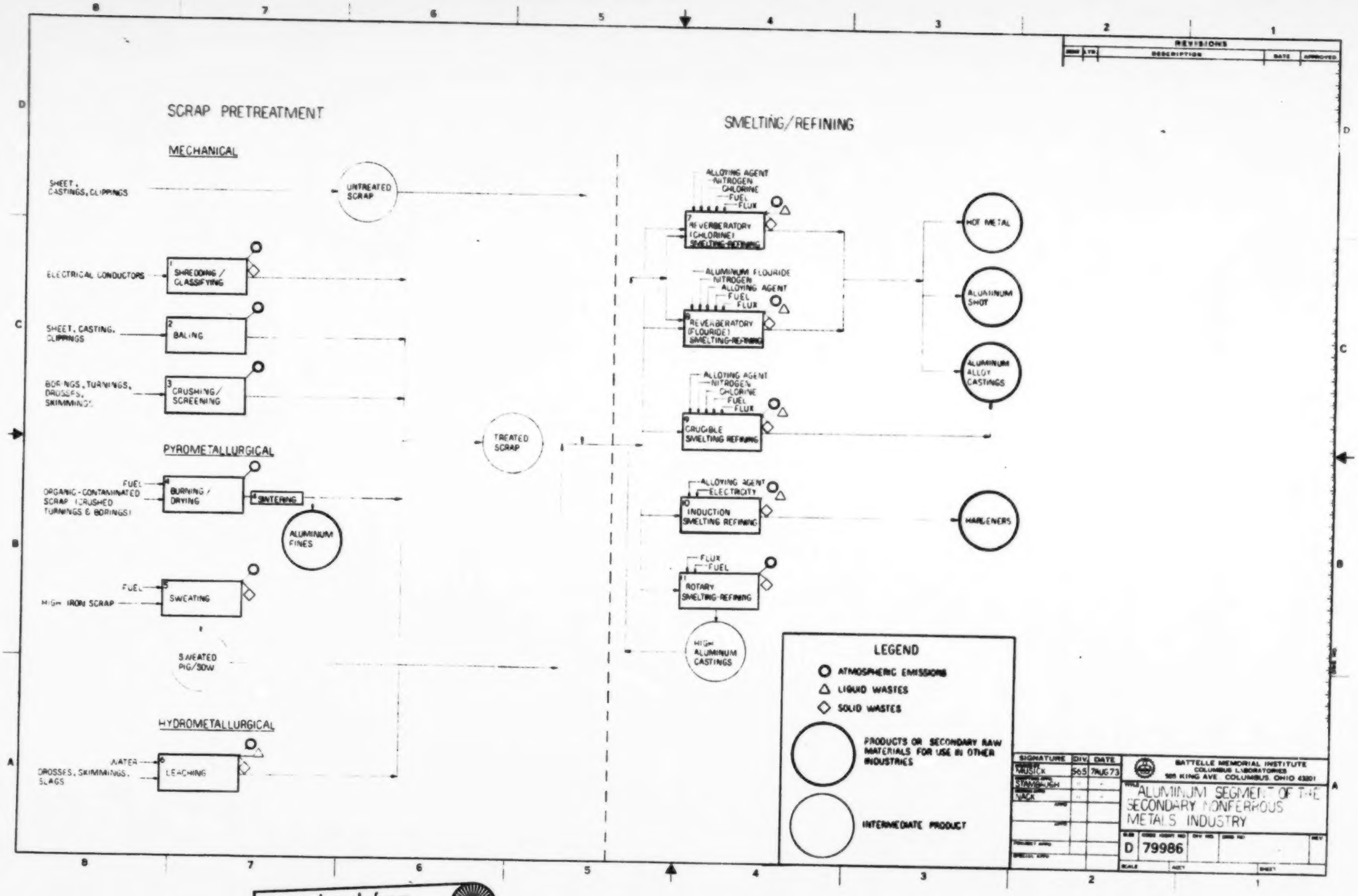
(31) Sonken-Galamba Corporation
Second and Riverview Streets
Kansas City, Kansas 66118
Telephone: (913) MA1-4100

(32) Superior Industries, Inc.
3790 Oakwood Avenue
Youngstown, Ohio 44509

(33) U. S. Aluminum Corporation of Pennsylvania
Railroad and Biddle Streets
Marietta, Pennsylvania
Telephone: 426-7811

(34) U. S. Reduction Company
Box 30
East Chicago, Indiana
Telephone: RE1-1000

(35) Wabash Smelting, Inc.
Post Office Box 453
Wabash, Indiana 46992


SCRAP PRETREATMENT
MECHANICAL
SHEET, CASTINGS, CLIPPINGS
UNTREATED SCRAP
ELECTRICAL CONDUCTORS
1 SHREDDING / CLASSIFYING
SHEET, CASTING, CLIPPINGS
2 BALING
BORINGS, TURNINGS, DROSSES, SKIMMINGS
3 CRUSHING / SCREENING
PYROMETALLURGICAL
FUEL
ORGANIC-CONTAMINATED SCRAP (CRUSHED TURNINGS & BORINGS)
4 BURNING / DRYING
SINTERING
ALUMINUM FINES
FUEL
HIGH IRON SCRAP
5 SWEATING
SWEATED PIG/SOW
HYDROMETALLURGICAL
WATER
DROSSES, SKIMMINGS, SLAGS
6 LEACHING
TREATED SCRAP
SMELTING/REFINING
ALLOYING AGENT
NITROGEN
CHLORINE
FUEL
FLUX
7 REVERBERATORY (CHLORINE) SMELTING-REFINING
ALUMINUM FLOURIDE
NITROGEN
ALLOYING AGENT
FUEL
FLUX
8 REVERBERATORY (FLOURIDE) SMELTING-REFINING
ALLOYING AGENT
NITROGEN
CHLORINE
FUEL
FLUX
9 CRUCIBLE SMELTING REFINING
ALLOYING AGENT
ELECTRICITY
10 INDUCTION SMELTING REFINING
FLUX
FUEL
11 ROTARY SMELTING-REFINING
HIGH ALUMINUM CASTINGS
HOT METAL
ALUMINUM SHOT
ALUMINUM ALLOY CASTINGS
HARDENERS
LEGEND
ATMOSPHERIC EMISSIONS
LIQUID WASTES
SOLID WASTES
PRODUCTS OR SECONDARY RAW MATERIALS FOR USE IN OTHER INDUSTRIES
INTERMEDIATE PRODUCT
REVISIONS
DESCRIPTION
DATE
APPROVED
SIGNATURE
DIV
DATE
MUSICK
565
7AUG73
STAMBAUGH
VACK
BATTELLE MEMORIAL INSTITUTE
COLUMBUS LABORATORIES
505 KING AVE. COLUMBUS, OHIO 43201
ALUMINUM SEGMENT OF THE SECONDARY NONFERROUS METALS INDUSTRY
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PROCESS DESCRIPTION OF THE ANTIMONY SEGMENT OF THE SECONDARY NONFERROUS METALS INDUSTRY

The secondary antimony segment recovers antimony as an alloy with lead rather than as pure metal because of the far greater demand for the alloy. Also, primary lead refineries recover the metal as antimonial lead. The bulk of the antimonial lead is used in storage battery grids and contains about 3 percent antimony.

Statistics for the secondary antimony industry for 1971 are presented below.

Kind of Scrap	Production, Short Tons	Form of Recovery	Production, Short Tons
New scrap	3,342	An antimonial lead	15,839
Old scrap	17,575	In other lead alloys	5,078*
Total scrap	20,917	Total recovery	20,917

* Includes 11 short tons in tin-base alloys.

Further, in 1971, by-product antimonial lead produced at primary lead refineries amounted to 19,686 tons containing 1,191 tons of antimony (6 percent).

Raw Materials

New scrap consisting of residues and drosses resulting from manufacturing and casting amounted to 16 percent of the total scrap processed in 1971. Old scrap, obtained mostly from used lead-acid type battery grids, amounted to the remaining 84 percent. Greater than 99 percent of both old and new scrap was in the form of lead-base alloys while less than 1 percent was comprised in tin-base alloys.

Although the increased useful life of batteries tended to reduce the quantity of available battery scrap, the trend was soon counterbalanced by the increase in the automobile population, thus insuring a continued supply of used battery grids as scrap. The raw materials to this industry, therefore, include:

(1) Old battery grids
(2) Residue and drosses from manufacturing and casting
(3) Scrap from the machining and manufacturing industry.

Products

Products from the antimony segment include:

(1) Antimonial lead alloys used in storage battery grids containing about 3 to 4 percent antimony (grid metal)
(2) Body solder used in automobile bodies
(3) Type metal used in printing. This alloy has 4-23 percent antimony, 17-30 percent tin, and the remaining is lead
(4) Master alloys containing large amounts of antimony (15 percent or more) and used in blending to manufacture other alloys
(5) Pure lead as a by-product.

Process Description

The recovery of antimony as alloy from scrap involves three manufacturing operations: (1) scrap pretreatment, (2) smelting, and (3) refining/casting. These operations and the major individual processes under each operation are shown on the flowsheet of this segment of the secondary nonferrous metals industry.

Scrap Pretreatment Operation

New scrap generated in machine shops is not pretreated. Old scrap from type and babbit metals is not only insignificant in quantity, but is generally not pretreated before smelting. However, since 70 percent of the old scrap is used battery scrap, pretreatment of these used batteries will be described. The flowsheet indicates a single scrap pretreatment process which is discussed below.

Battery Breaking, Crushing, and Hydroseparation Process (1). This process which separates the metallic parts of the old battery from the plastic and rubber portions is conducted in one of two ways. The more common method, adopted by about 75 percent of the industry, consists of the following steps: (a) mechanical sawing of the top of the battery, (b) manually separating the bottom case from the acid and grids by dumping, (c) cleaning grids by water spray, (d) crushing the battery tops and separating the metals on a vibratory table, (e) crushing the bottom case in a hammer mill for disposal in landfills, and (f) neutralizing the acid effluent from dump tanks with lime in a settling pond.

The second method, used in about 25 percent of the industry, consists of the following process steps: (a) crush the whole battery (as received) in a hammer mill, (b) drain and treat the acid, and (c) conduct heavy media separation to separate plastics from the lead oxide and lead metal. This process produces a richer feed to smelters.

Energy requirements for this process are electrical energy for the vibratory feeder, the hammer mill, and the heavy media separation column.

The wastes generated are about the same in both processes and consist of: (1) acidified (sulfuric) wastewater, (2) shredded plastic and rubber, and (3) fine particles of metal and plastics as ambient air emissions from the hammer mill and vibrating table.

The potential for pollution from these wastes is greatly reduced by the following waste treatment processes in current use: (1) neutralization of acid wastewater with dolomitic lime (CaO) in a settling pond and (2) landfilling or utilization of shredded plastics in road surfacing and to produce nonleaching landfill material.(1) As a result of these waste treatment steps, this process does not have much pollution potential. If the treatment steps are not adopted, the pollution can be serious.

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(1) John A. Bitler and L. John Minnick, "Lime-Sulfur Dioxide Scrubbing System and Technology for Utilization of Underflow Sludge", Industrial Wastes, March/April 1973.

Smelting Operation

This operation consists of two processes which are described below.

Reverberatory Smelting Process (2). This process melts, purifies, and separates the metallic portions of the feed scrap generated in the pretreatment steps. The process steps are: (a) charging the furnace, (b) melting the charge, (c) pouring out the lead metal, and (d) removing the slag.

Energy required is from the fuel oil to operate the furnace and from electricity to operate the auxiliary equipment.

Wastes from the process are atmospheric emissions containing flue dust and sulfur oxides and liquid wastes.

These wastes are treated effectively. The flue dust has sufficient lead metal value to warrant almost complete recovery for which purpose a baghouse is used. The collected dust is recycled to the furnace. The sulfur oxides are scrubbed with dolomitic lime and the resulting sludge (calcium-magnesium sulfates) is used in road surfacing or in preparing nonleachable landfill material.

The pollution potential of this process can be serious if the pollution control systems are not properly maintained.

Blast Furnace Smelting Process (3). The blast furnace produces lead metal with a high antimony content and also reduces the oxides of lead and antimony to their respective metals. The feed to this furnace includes slag from the reverberatory furnace.

The process steps are: (a) continuous charging of coke, slag, and treated battery scrap; (b) heating with blasts of air, and (c) withdrawing the metal and slag.

Heat energy in the form of coke is the main requirement of the process.

The wastes produced are: atmospheric emissions containing flue dust and flue gas rich in sulfur oxides, solid waste as blast furnace slag, and liquid waste as waste cooling water.

The atmospheric emissions are treated by the same method used for emissions from the reverberatory smelting process. The slag is probably disposed of in a landfill.

The process has the potential for producing serious pollution problems if the emissions are not controlled and if collected wastes are not disposed of in a nonpolluting manner.

Refining and Casting Operation

Pot Molding and Casting Process (4). In this process, the metal products from the reverberatory and blast furnaces are molded after adjusting to required alloy compositions. Air blowing is done if removal of all antimony is desired.

The process steps are: (a) charging the furnace, (b) melting the charge, (c) blowing if necessary, (d) pouring the molten metal into the molds, and (e) casting the metal into ingots.

Heat energy is the main requirement.

The wastes are mainly atmospheric emissions containing gases and metal oxides, dust, and fume. An afterburner burns incinerable fumes and a baghouse collects the dust and the metal oxides. Finally, the scrubber takes out acidic oxides before the off gases are vented to the atmosphere.

Due to current flue gas treatment employed, the process has little pollution potential. However, if not controlled, the process could be a source of pollution problems.

Population of Secondary Antimony Processors

(1) Allie Smelting Corporation
5116 W. Lincoln Avenue
Milwaukee, Wisconsin 53219
Telephone: (414) 541-7830

(2) Dixie Lead Company, Inc.
Post Office Box 8625
Dallas, Texas 75216
Telephone: WA6-2132

(3) Electric Storage and Battery Company
2 Penn Central Plaza
Phildelphia, Pennsylvania

(4) Florida Smelting Company
2640 Capitola Street
Jacksonville, Florida
Telephone: (904) 353-4317

(5) Frankel Company, Inc.
19300 Filer Avenue
Detroit, Michigan
Telephone: SO6-5300

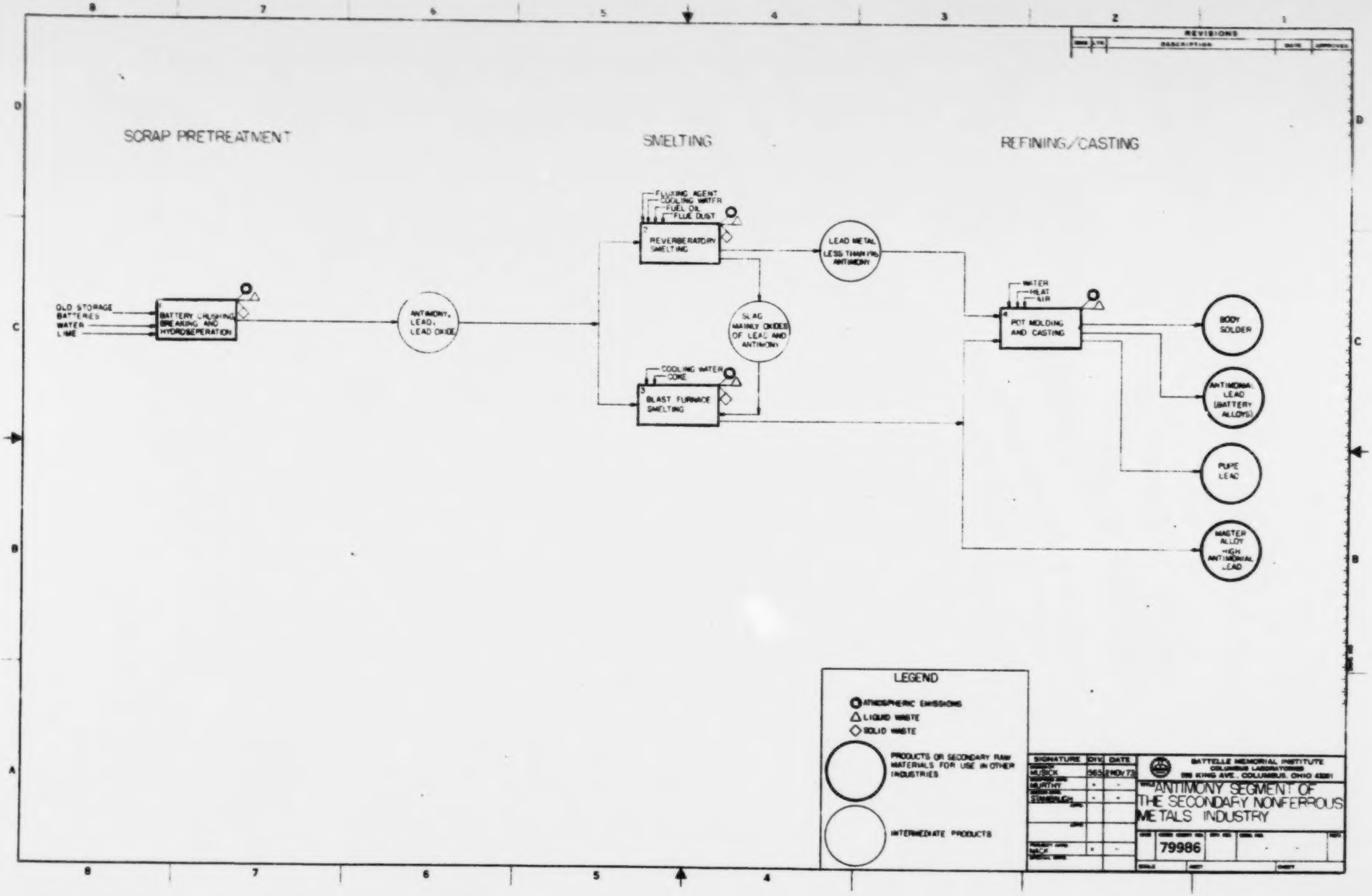
(6) General Battery Corporation
Post Office Box 1262
Reading, Pennsylvania

(7) Inland Metals and Refining Company
651 E. 119th Street
Chicago, Illinois 60628
Telephone: (312) 928-6767

(8) Seitzinger's, Inc.
900 Ashby Street NW
Atlanta, Georgia 30301
Telephone: (404) 876-3787

(9) U.S.S. Lead Refinery, Inc.
5300 Kennedy Avenue
East Chicago, Indiana
Telephone: (219) 397-1012

(10) Hyman Veiner & Sons
Post Office Box 573
Richmond, Virginia 23205
Telephone: (703) 648-6563


SCRAP PRETREATMENT
SMELTING
REFINING/CASTING
OLD STORAGE BATTERIES
WATER
LIME
1 BATTERY CRUSHING BREAKING AND HYDROSEPERATION
ANTIMONY, LEAD, LEAD OXIDE
FLUXING AGENT
COOLING WATER
FUEL OIL
FLUE DUST
2 REVERBERATORY SMELTING
COOLING WATER
COKE
3 BLAST FURNACE SMELTING
SLAG MAINLY OXIDES OF LEAD AND ANTIMONY
LEAD METAL LESS THAN 1% ANTIMONY
WATER
HEAT
AIR
4 POT MOLDING AND CASTING
BODY SOLDER
ANTIMONIAL LEAD (BATTERY ALLOYS)
PURE LEAD
MASTER ALLOY HIGH ANTIMONIAL LEAD
LEGEND
ATMOSPHERIC EMISSIONS
LIQUID WASTE
SOLID WASTE
PRODUCTS OR SECONDARY RAW MATERIALS FOR USE IN OTHER INDUSTRIES
INTERMEDIATE PRODUCTS
REVISIONS
DESCRIPTION
DATE
APPROVED
SIGNATURE
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MURTHY
STANBAUGH
NACK
BATTELLE MEMORIAL INSTITUTE
COLUMBUS LABORATORIES
505 KING AVE., COLUMBUS, OHIO 43201
ANTIMONY SEGMENT OF THE SECONDARY NONFERROUS METALS INDUSTRY
79986

PROCESS DESCRIPTION OF THE BERYLLIUM SEGMENT OF THE SECONDARY NONFERROUS METALS INDUSTRY

Beryllium, like indium, is a very expensive metal with a current market value of about $6 per ounce. Total U. S. production of beryllium can be estimated at less than 500 tons per year. Exact production figures are a trade secret and no data on secondary production are available. In fact, there is no distinct secondary segment because most of the scrap is generated in-house.

Raw Materials

Details of raw materials to this industry are not available. Tonnagewise, the raw material availability is estimated at less than 100 tons per year.

Products

Pure beryllium metal and alloys of beryllium with copper are some of the products.

Process Description

There are only two beryllium processors in the U. S. They are not willing to reveal the process steps because of the competitive nature of the industry and the need to protect the proprietary nature of their process.

Also, a discussion of the process will not be of much avail because both the processors feel that it would not be in their best interest to obtain R&D assistance from external agencies, either public or private. The companies conduct their research in-house.

The following information provided by one of the companies is reported for record.

(1) Scrap beryllium is treated by pyrometallurgical methods to produce pure metal. Typically, vacuum casting followed by hot pressing and grinding are used.

(2) Excellent hooding and bag fillers where necessary are used to prevent escape of beryllium.

(3) Beryllium inhalation produces effects akin to silicosis and, therefore, extreme care is taken to minimize the indoor and ambient concentration of this metal.

(4) The company has no problems that they cannot solve by their own efforts.

Population of Secondary Beryllium Processors

(1) Brush Wellman Engineered Materials
17876 St. Clair Avenue
Cleveland, Ohio 44110
Telephone: (216) 486-4200

(2) Kawecki Berylco Industries, Inc.
220 East 42nd Street
New York, New York 10017
Telephone: (212) 682-7143

PROCESS DESCRIPTION OF THE BRASS AND BRONZE SEGMENT OF THE SECONDARY NONFERROUS METALS INDUSTRY

Introduction

The brass and bronze segment constitutes a large portion of the secondary nonferrous metals industry. Since World War II, the production of brass and bronze ingots in the United States has been fairly constant, averaging slightly over 300,000 tons annually. In 1969, the production rate was 326,000 tons. Potential environmental pollutants from this industry are atmospheric emissions, both gases and particulate matter, liquid wastes, and solid wastes, which if not controlled and properly disposed of can result in serious pollution problems. Emission potential of particulates alone has been estimated at 10,000 tons annually, based on an annual production of 300,000 tons of ingots.

Raw Materials

Obsolete domestic and industrial copper-bearing scrap is the basic raw material of the brass and bronze segment. About two-thirds of the scrap is in the form of brasses and bronzes; the other one-third is received in the form of copper scrap. Of the many hundreds of copper-base alloys that become available for reuse through scrap recovery channels, 54 primary types of copper-bearing scrap are now included in the standards published by the National Association of Secondary Materials Industries.(1) These are listed in Table 1.

Scrap as received is frequently not clean and may contain any number of undesirable metallic and nonmetallic impurities that contribute nothing to the composition of the ingot but increase the problems in producing high quality products. Among these undesirable constituents are oil, grease, paint, insulation, rubber, and antifreeze.

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(1) Bulletin NF-66, National Association of Secondary Materials Industry, 330 Madison Avenue, New York, New York.

TABLE C-1. TYPES OF COPPER-BEARING SCRAP

No.	Designation
1.	No. 1 copper wire
2.	No. 2 copper wire
3.	No. 1 heavy copper
4.	Mixed heavy copper
5.	Light copper
6.	Composition or red brass
7.	Red brass composition turnings
8.	Genuine babbitt-lined brass bushings
9.	High-grade, low-lead bronze solids
10.	Bronze papermill wire cloth
11.	High-lead bronze solids and borings
12.	Machinery or hard red brass solids
13.	Unlined standard red car boxes (clean journals)
14.	Lined standard red car boxes (lined journals)
15.	Cocks and faucets
16.	Mixed brass screens
17.	Yellow brass scrap
18.	Yellow brass castings
19.	Old rolled brass
20.	New brass clippings
21.	Brass shell cases without primers
22.	Brass shell cases with primers
23.	Brass small arms and rifle shells, clean fired
24.	Brass small arms and rifle shells, clean muffled (popped)
25.	Yellow brass primer
26.	Brass pipe
27.	Yellow brass rod turnings
28.	Yellow brass rod ends
29.	Yellow brass turnings
30.	Mixed unsweated auto radiators
31.	Admiralty brass condenser tubes
32.	Aluminum brass condenser tubes
33.	Muntz metal tubes
34.	Plated rolled brass
35.	Manganese bronze solids
36.	New cupro-nickel clippings and solids
37.	Old cupro-nickel solids
38.	Soldered cupro-nickel solids
39.	Cupro-nickel turnings and borings
40.	Miscellaneous nickel copper and nickel-copper-iron scrap
41.	New monel clippings and solids
42.	Monel rods and forgings
43.	Old monel sheet and solids
44.	Soldered monel sheet and solids
45.	Soldered monel wire, screen, and cloth
46.	New monel wire, screen, and cloth
47.	Monel castings
48.	Monel turnings and borings
49.	Mixed nickel silver clippings
50.	New nickel silver clippings and solids
51.	New segregated nickel silver clippings
52.	Old nickel silver
53.	Nickel silver castings
54.	Nickel silver turnings

Products

The products from the brass and bronze segment of the secondary nonferrous metals industry are hardeners and brass and bronze alloy ingots. Brass and bronze are copper-base alloys with zinc and tin, respectively, as the largest secondary component. Other alloy agents may include such elements as lead, iron, aluminum, nickel, silicon, or manganese. Members of the Brass and Bronze Ingot Institute produce 31 standard copper-base alloys as shown in Table 2.

TABLE C-2. NOMINAL CHEMICAL SPECIFICATIONS FOR BBII STANDARD ALLOYS

Alloy No.	Classification	Cu, %	Sn, %	Pb, %	Zn, %	Fe, %	Al, %	Ni, %	Si, %	Mn, %
1A	Tin bronze	88.0	10.0		2.0					
1B	Tin bronze	88.0	8.0		4.0					
2A	Leaded tin bronze	88.0	6.0	1.5	4.0					
2B	Leaded tin bronze	87.0	8.0	1.0	4.0					
2C	Leaded tin bronze	87.0	10.0	1.0	2.0					
3A	High-lead tin bronze	80.0	10.0	10.0						
3B	High-lead tin bronze	83.0	7.0	7.0	3.0					
3C	High-lead tin bronze	85.0	5.0	9.0	1.0					
3D	High-lead tin bronze	78.0	7.0	15.0						
3E	High-lead tin bronze	71.0	5.0	24.0						
4A	Leaded red brass	85.0	5.0	5.0	5.0					
4B	Leaded red brass	83.0	4.0	6.0	7.0					
5A	Leaded semi-red brass	81.0	3.0	7.0	9.0					
5B	Leaded semi-red brass	76.0	2.5	6.5	15.0					
6A	Leaded yellow brass	72.0	1.0	3.0	24.0					
6B	Leaded yellow brass	67.0	1.0	3.0	29.0					
6C	Leaded yellow brass	61.0	1.0	1.0	37.0					
7A	Manganese bronze	59.0	1.0	1.0	37.0	1.0	0.6			0.5
8A	Hi-strength mang. bronze	57.5			39.0	1.0	1.0			1.5
8B	Hi-strength mang. bronze	64.0			24.0	3.0	5.0			3.5
8C	Hi-strength mang. bronze	64.0			24.0	3.0	5.0			3.5
9A	Aluminum bronze	88.0				3.0	9.0			
9B	Aluminum bronze	89.0				1.0	10.0			
9C	Aluminum bronze	85.0				4.0	11.0	2.0		0.5
9D	Aluminum bronze	81.0				4.0	11.0	4.0		3.0
10A	Leaded nickel brass	57.0	2.0	9.0	20.0			12.0		
10B	Leaded nickel brass	60.0	3.0	5.0	16.0			16.0		
11A	Leaded nickel bronze	64.0	4.0	4.0	8.0			20.0		
11B	Leaded nickel bronze	66.5	5.0	1.5	2.0			25.0		
12A	Silicon bronze	88.0			5.0	1.5			4.0	1.5
12B	Silicon brass	82.0			14.0				4.0	

Process Description

The production of brass and bronze products using scrap as the basic source of raw material entails two manufacturing operations: (1) scrap pretreatment and (2) smelting-refining. The two manufacturing operations and the individual processes under each operation are shown in the attached flowsheet entitled "Brass and Bronze Segment of the Secondary Nonferrous Metals Industry".

Scrap-Pretreatment Operation

Before the scrap is blended in a furnace to produce the alloy of a desired composition, removal of some of the metallic and nonmetallic impurities or contaminants and densification of the scrap are conducted to produce a material more suitable for subsequent smelting-refining. The pretreatment process employed depends upon the type of scrap as noted in the flowsheet by Numbers 1 through 9.

Stripping Process (1). Insulation is removed from electrical conductors such as cables by specially designed stripping machines or by hand.

Energy demand is that needed to drive the equipment.

Essentially no atmospheric emissions or liquid wastes are generated by this process. However, significant quantities of solid wastes are produced. These wastes consist of primarily organic materials such as plastics and other materials used as protective coverings on copper scrap.

The pollutants generated are expected to cause no atmospheric pollution problems, unless the solid wastes are disposed of by burning. Disposal of the solid wastes in landfills may possibly cause water pollution if the landfill is not properly prepared.

Briquetting Process (2). Compressing the bulky scrap such as borings, turnings, and wire into small bales densifies the scrap, permits more compact storage, and makes for easier handling and faster melting. Briquetting is carried out by compacting the scrap with hydraulic presses.

Energy required is that to drive the equipment.

Essentially no atmospheric emissions and no liquid or solid wastes are generated.

The process has little or no potential for the production of pollution problems.

Shredding Process (3). The shredding process also achieves separation of the insulation from the copper-bearing scrap. The process steps are: (a) introducing the insulated copper scrap such as copper wire into a hammermill where the scrap is cut into small pieces and the insulation is broken loose from the metal, and (b) removing the insulation by air classification. This process is used in larger plants because of high capital costs.

Energy demand is that required to drive the equipment.

Potential environmental pollutants from this process are atmospheric emissions (gases and particulate matter) and solid wastes. The atmospheric emissions are the fine particulate matter composed of the insulation and fine metal particles and the gas, generally air, used in the classification. The air is not a pollutant; however, the particulate matter is a potential pollutant if not collected and disposed of properly. Cyclones are used as the pollution abatement device. Solid wastes are the insulation and metal particles removed from the scrap by the air classification.

The process has the potential for creating environmental pollution problems. The fine particulates may cause atmospheric pollution problems; the solid wastes may cause water pollution problems if not disposed of in an approved landfill.

Magnetizing Process (4). The scrap may be a mixture of ferrous as well as nonferrous components. The ferrous component of the scrap is removed by the magnetizing process which entails passing the scrap over magnetized pulleys. Scrap treated in this manner is brass borings and small items.

Energy required is limited to that to drive the equipment.

The only wastes generated by this process are solid wastes--scrap iron which may be contaminated with other metals and organic compounds such as the machining oils. These are disposed of by either landfill or selling to a ferrous scrap dealer.

The process has essentially no potential for the production of a pollution problem.

Sweating Process (5). Much of the scrap such as radiators contains low melting components such as lead, solder, and babbitt metal. These are removed from the scrap by the sweating process which entails heating the scrap in a furnace. The process steps are: (a) charging the furnace, (b) melting the low-melting components, (c) collecting the melt, and (d) removing the treated scrap from the furnace for further processing. The collected metal may be made into white alloys, used for lead and tin addition to the copper base alloys, or sold as produced to a refinery.

Energy required includes the fuel to fire the furnace and electricity to drive the equipment. Several types of furnaces--rotary kiln, tunnel furnace, pot furnace, or reverberatory furnace--may be used. Both gas and oil are potential sources of fuel, depending on the availability and type of furnace.

Environmental pollutants generated by this process are: atmospheric emissions, solid wastes, and possibly aqueous wastes. Atmospheric emissions contain primarily fumes and combustion products of antifreeze residues, soldering salts, hose connections, and fuel. Metal content of the emissions is expected to be low because of the low sweating temperature. Solid wastes are those from the pollution abatement equipment. If wet scrubbers are used to reduce atmosphere pollution, liquid wastes are generated.(2)

The process is a potential source of serious atmospheric pollution and presents potential pollution problems resulting from disposal of the solid wastes and liquid wastes, if generated.

Burning Process (6). Much of the scrap is covered with insulation such as polyethylene, polypropylene, or polyvinyl chloride. These contaminants are removed from the scrap by the burning process using such furnaces as muffles and rotary kilns. The process steps are: (a) charging the furnace, and (b) burning off the organic contaminants. Whereupon, the pretreated scrap is removed from the furnace for further processing.

Energy required is the fuel--gas or oil--to heat the furnaces and electricity to drive the equipment.

The burning process is a potential source of serious pollution problems. Burning of the organic contaminants in the scrap results in atmospheric pollution problems. In addition to the combustion products such as carbon dioxide and water, the emissions may contain such gases as phthalic anhydride and hydrogen chloride from the burning of, for example, polyvinyl chloride. Fluorocarbon insulation releases hydrogen fluoride when burned. Many of these gases are highly toxic and corrosive.

Little information is available on these emissions. Source tests in Los Angeles indicate that uncontrolled emissions can be dense black smoke containing particulate matter in concentrations as large as 29 grains/scf at 12 percent carbon dioxide. These particulates must have been primarily carbon, because burning the emissions at 2000 F

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(2) Schwartz, H. E., Kramer, H., and Company, Controlling Atmospheric Contaminants in the Smelting and Refining of Copper-Base Alloys, J. APCA, V5 N1, May, 1955.

(probably in an afterburner) reduced the particulate matter level to 0.16 grains/scf at 12 percent carbon dioxide.(3)

Solid and liquid wastes are not generated by the process; however, both may be generated by the pollution control devices. Disposal of these materials is probably by landfill and settling ponds, respectively.

Drying Process (7). Borings, turnings, and chips from machining are covered with cutting fluids, oils, and greases. These contaminants are removed in the drying process, where the scrap is heated in, for example, a rotary kiln to vaporize the contaminants.

Energy required is the fuel to heat the furnace and drive the equipment. Fuel used in this case may be oil or gas.

Drying results in the evolution of considerable quantities of hydrocarbons depending on the amount present in the scrap. In addition, the oils, greases, and cutting fluids contain sulfonated and chlorinated hydrocarbons. Therefore, the gaseous emissions are composed of sulfur oxides, hydrogen chloride, hydrocarbons, and other combustion products. Particulate matter in the atmospheric emissions is soot and possible metallic fumes. Essentially no solid or liquid wastes are generated by the process.

The atmospheric emissions are controlled by burning the vaporized fumes in afterburners to oxidize the hydrocarbons to carbon dioxide and water. However, this technique does not remove the sulfur oxides and chloride emissions. Wet scrubbing is required.

This process can present atmospheric pollution problems, if the emissions are not controlled.

Cupolaing Process (8). This process densifies bulky scrap and recovers metal values from slags, skimmings, and other low copper scrap to produce cupola melt (black copper) which is refined to produce the finished alloy. The process steps are: (a) charging of the cupola, (b) melting the charge, and (c) removing the slag. Afterwards, the cupola melt is poured and cast. The charge is made up of coke, flux, and the copper-containing scrap. Air is introduced through tuyeres around the bottom of the shaft. Coke is used both as a fuel and as a reducing agent. Limestone or other materials is used for fluxing. Slag and concentrated alloy (cupola melt) are tapped near the bottom of the furnace.

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(3) Air Pollution Engineering Manual, Air Pollution Control District, County of Los Angeles, Public Health Service Publication No. 999-AP-40, pp 270-284, 1967.

Energy required for this process is coke which is used both as a fuel and as a reducing agent.

The process produces: (a) atmospheric emissions containing both gases and particulate matter (fume and dust), (b) liquid wastes, and (c) solid wastes. The composition of the particulate matter and gases from the cupola are variable because of the wide variety of scrap, slag, and skimmings added as the source of alloy and the various fluxes used. However, it is expected that the particulate matter will contain such metal values as zinc, lead, tin, copper, silicon, manganese, and some unburned coke, with the majority of the emissions being zinc because of its high vapor pressure at the cupolaing temperatures. The gases are expected to contain, in addition to the combustion products, such materials as sulfur oxides and halides.

Emission rates also vary because of the wide variation in the charge composition. For example, raw emission factors (furnace emission factors) were reported to range from 16.7 to 73.2 lb of particulate matter per ton of feed. Using a baghouse with a collection efficiency of 96.4 percent as the pollution control device, emission factors were reduced to within 0.9 to 4.1 lb of dust per ton of feed.(4)

Since zinc oxide is normally the major component in the fume, particle shape is generally acicular, i.e., long needles with a large length to width ratio (~5 to 1). This shape is characteristic of zinc oxide. In some cases, the particle resembles a wheel with the rim removed. Particle size ranges from 0.03 to 0.3 micron which makes collection very difficult. The dust particles have an irregular shape and are expected to be much larger, possibly in the 5 to 10 micron range.(5)

---

(4) Air Pollution Aspects of Brass and Bronze Smelting Refining Industry, U. S. Dept. HEW, NAPCA, Publication No. AP-58, Raleigh, North Carolina (1969).

Liquid wastes are generated primarily as cooling wastewater from water-quenching of the slag and from cooling of the cupola. Solid wastes generated by this process are slags, fumes and dusts collected in the baghouse, spills, and sweepings. The wastewater is disposed of in settling ponds, recycled, or sent to sewers or nearby streams. Some of the solid wastes are recycled; others are discarded.

Atmospheric emissions and liquid and solid wastes generated by the cupola can result in serious pollution problems.

Gravity Concentration Process (9). Metallic values are recovered from slags, drosses, skimmings, spills, and sweepings by the gravity concentration process, whereby the heavy (more dense) particles settle faster than the lighter particles in a water medium. The process steps are: (a) grinding, (b) screening, and (c) gravity separation in a water medium.

Energy required is that necessary to drive the equipment.

Only minor quantities of atmospheric emissions are expected from the gravity separation process. These are generated in the crushing and screening steps. However, large quantities of liquid wastes containing both suspended and dissolved solids are generated in the gravity separation step. The liquid wastes are probably treated in settling ponds and the water recycled or discharged to sewers or streams.

This process does not pose an atmospheric pollution problem; however, if not controlled, liquid and solid wastes could cause water pollution problems.

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(5) Air Pollution Engineering Manual, Air Pollution Control District, County of Los Angeles, Public Health Service Publication No. 999-AP-40, pp 185-186, 1967.

Smelting-Refining Operation

Pretreatment of the scrap removes a portion of the metallic and nonmetallic impurities found in scrap and physically prepares the material for further processing by the smelting-refining manufacturing operation. In this operation, additional metallic and nonmetallic impurities are removed and the composition of the alloys adjusted to produce alloy ingots of the desired specifications. The processes employed to produce the alloy ingots are discussed in the sections below and shown on the flowsheet by Numbers 10 through 13.

Reverberatory Smelting-Refining Process (10). Brass and bronze alloys of desired specifications are produced by the reverberatory smelting-refining process. This is achieved by the removal of metallic and nonmetallic impurities from pretreated scrap and by the addition of alloying agents. The process steps are: (a) charging of the reverberatory furnace, (b) melting of the charge, (c) fluxing to remove the impurities, (d) alloying to adjust the composition of the melt, (e) pouring of the molten alloy, and (f) casting of the molten alloy into ingots.

This process produces large quantities of atmospheric emissions and liquid and solid wastes. The atmospheric emissions are composed of gases and particulate matter. The particulate matter includes such materials as carbon particles, entrained dust, unburned fuel, and metallic fumes. The gases in the atmospheric emissions include carbon dioxide and carbon monoxide from combustion of the fuel, sulfur oxides, halogens, and nitrogen oxides. Each processing step is a source of atmospheric emissions.

Charging is a major source of atmospheric emissions from the reverberatory smelting-refining process. The type and condition of the scrap are factors that affect the quantity and composition of the emissions. If the scrap is oily, the emissions will contain, in addition to the combustion products, unburned hydrocarbons and dust particles. When the scrap contains large quantities of highly volatile constituents such as zinc, heavy evolution of fumes will occur.

Emissions are also dependent upon factors such as location of the charging doors and method of charging. Overhead charging results in heavy evolution of emissions containing both gases and particulate matter. End and side charging results in lower emissions. Batch charging produces large bursts of emissions that are almost impossible to control.

Melting of the charge is another major source of atmospheric emissions from this process. These emissions contain larger proportions of metallic fumes than those from the charging step.

Emissions data are not available for each individual step. However, data collected in an earlier survey of industry(6) revealed that particulate emission factors for charging-melting ranges from 11.7 to 59.0 lb/ton of feed charged to the furnace. These particulate emissions contained, in some cases, 60 to 90 percent zinc, probably as zinc oxide; in other cases, the particulate emissions contained 33.7 to 73.6 percent nonmetallic materials, 16.7 to 52.8 percent zinc, probably as zinc oxide, and 0.38 to 4.62 percent copper. No doubt, the particulate emissions also contained trace quantities of other metallic materials such as lead and cadmium.

Emission factors are not available for the gaseous emissions. However, large volumes of gases are evolved from combustion of the fuel and other sources.

Reported particle size also varied over a wide range, possibly because the extremely fine particles may have passed through the filter medium used to collect the samples. In any event, particle sizes were reported to be less than 20 microns in some cases and in others, less than 1 micron.

The fluxing process step is a purification or smelting-refining step, whereby impurities are removed from the melt. These materials are removed by the addition of gaseous, liquid, or solid fluxes. Consequently, fluxing can be a major source of atmospheric emissions, especially in those cases where gaseous fluxes are used. These emissions may contain a wide variety of metallic constituents such as iron, manganese, silicon, aluminum, copper, zinc, and lead, along with those materials from the flux. These emissions may be volatilized from the melt as fume or carried from the melt by entrainment in the gaseous emissions. Emission factors for this step are not available.

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(6) Survey conducted by Battelle's Columbus Laboratories.

In the alloying step, virgin metal or specialized scrap is added to adjust the composition of the melt. Normally, this step is not a major source of atmospheric emissions, unless high zinc alloys are being produced. In this case, large quantities of zinc fumes may be emitted.

Metal oxide fumes are produced as the hot metal is poured through the air into the molds. Other emissions are also produced, depending on the type of linings or coverings associated with the mold as it is filled with hot metal. Thus, the pouring step can be a significant source of atmospheric emissions and will vary depending on such factors as composition of the alloy, pouring temperature, pouring rate, and type of molds. Raw particulate emission factors collected in an earlier survey were noted to range from 0.4 to 10.9 lb of dust per ton of product. These emissions contained a high zinc content; in one case, 60 to 90 percent.

Casting is a minor source of atmospheric emissions.

Thus, the reverberatory smelting-refining process for the production of brass and bronze ingots is a major source of atmospheric emissions. Raw particulate emissions factors (including both fumes and dusts) range from 125 to 140 lb per ton of feed. Composition will vary but, in general, the emissions will contain both metallic and nonmetallic constituents. The metallic emissions are composed of, in addition to a high concentration of zinc, varying concentrations of lead, tin, copper, silicon, and other metal values. In one case,(6) the dust collected in a brass and bronze smelter baghouse contained 45.0 to 77.0 percent zinc, 1.0 to 12.0 percent lead, 0.3 to 2.0 percent tin, 0.05 to 1.0 percent copper, 0.5 to 1.5 percent chlorine, and 0.1 to 0.7 percent sulfur. Gaseous emissions contain, in addition to the combustion products, volatilized organic materials such as oil and grease, sulfur oxides, nitrogen oxides, and hydrogen halides such as hydrogen chloride. The baghouse is the most widely used pollution abatement device.

Liquid wastes generated by this process are primarily cooling wastewater. One source is cooling of the ingots by a water spray.

Significant quantities of solid wastes--slags, flue dusts, and baghouse dusts--are generated by this process. In one case,(7) 10,000 lb of slag and 4,000 lb of flue dust were generated in the production of 178,000 lb of brass ingot product. Losses designated as gases, dusts, and others were estimated at 1,600 lb.

Thus, the reverberatory smelting-refining process produces large quantities of potential environmental pollutants. Therefore, this process has the potential for the production of serious pollution problems.

Rotary Smelting-Refining Process (11). This process, like the reverberatory smelting-refining process, produces brass and bronze ingots from the various types of scrap. Capacity of the rotary furnace used in this process ranges from several tons to approximately 50 tons of nonferrous metals. The process steps are: (a) charging of the scrap through ports on the side of the cylinder, (b) melting of the charge, (c) fluxing to remove impurities, and (d) alloying to adjust composition of the melt. Afterwards, the melt is poured and cast into ingots.

Energy required is the fuel used in the various process steps and electricity to drive the equipment. The rotary furnace is direct-fired using oil or gas as the fuel.

The process produces significant quantities of atmospheric emissions, liquid wastes, and solid wastes. The atmospheric emissions are generated in each of the process steps. Since the rotary smelting-refining process is similar to the reverberatory smelting-refining process in that both are direct-fired and the same process steps are employed, the quantity, composition, and particle morphology of emissions are comparable. For example, the raw emissions factor for the rotary smelting-refining process was reported to be 147 lb of particulate matter per ton of feed, whereas the factor for the reverberatory smelting-refining process was reported to be 156.9 lb of particulate matter per ton of feed.

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(7) Spendlove, Max J., Methods for Producing Secondary Copper, U. S. Dept. of Interior, Bureau of Mines, Bureau of Mines IC8002 (1961).

Liquid wastes generated by this process are the wastewater from cooling of the ingots during casting. Solid wastes include wastes such as slag and baghouse dusts.

Thus, the process has a high potential for the production of serious pollution problems if emissions are not controlled.

Crucible Smelting-Refining (12). The crucible smelting-refining process is employed for producing brass and bronze alloys from clean, well segregated scrap and for refining specialized alloys. The process steps are the same for this process as for the other smelting-refining processes.

Energy required is the fuel necessary to fire the furnace and the electricity to drive the equipment. The furnace is indirect fired using gas or oil as the source of fuel; thus, the charge never comes in contact with the flame.

The process produces a modest quantity of potential environmental pollutants. Atmospheric emissions are generated in each processing step but at a rate significantly less than for the reverberatory smelting-refining process. For example, furnace emissions factor for crucible-smelting-refining was reported to range from 6.5 to 12.3* lb of fume per ton of feed(8), whereas furnace emissions factor for reverberatory smelting-refining was reported to range from 125 to 140 lb of dust per ton of feed(9). Using baghouses with collection efficiencies of 93.7 percent and 96.2 percent, respectively, the atmospheric emissions were lowered to 0.24 lb per ton of feed for the low zinc alloy and 0.80 lb per ton of feed for the high zinc alloy. Liquid wastes are generated in the casting of the ingots. Solid wastes generated by this process include slags and baghouse dusts. Composition and particle morphology of atmospheric emissions and composition of the liquid and solid wastes should be comparable to those from the other smelting-refining processes.

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(8) Air Pollution Engineering Manual, Air Pollution Control District, County of Los Angeles, Public Health Service Publication No. 999-AP-40-, p 274, 1967.

(9) Industry survey.

* Higher emissions factor resulted from high zinc content in the melt (24.8 percent vs. 3.8 percent).

Although this process produces significantly less potential environmental pollutants than the above smelting-refining processes, improper disposal of the pollutants and/or emitting them to the environment can result in atmospheric and water pollution problems.

Electric Crucible Smelting-Refining Process (13). This process is used to produce special high-grade brass and bronze alloys from treated scrap. The process involves the same process steps as employed in the other smelting-refining processes.

Energy required is the electricity to drive the equipment and process the alloy.

Electric crucible smelting-refining produces significant quantities of atmospheric emissions, solid wastes, and liquid wastes. These emissions and wastes are generated in the same processing steps as in the other processes. Also, the composition will be similar. The primary difference is the atmospheric emissions do not contain combustion products since the source of heat for the electric smelting-refining process is electricity rather than fossil fuels. Thus, the quantity of atmospheric emissions, including both gases and particulate matter, are significantly reduced. Data are not available for the gaseous emissions. However, furnace particulate emission factor was reported to be approximately 2.6 lb per ton of feed.(8) The baghouse removed 96.0 percent of the particulates.* Other wastes generated by the electric crucible smelting-refining process include liquid wastes from cooling of the ingots during casting and solid wastes such as slags and baghouse dusts.

Although this process emits significantly less particulate matter than other smelting-refining processes, there is the potential for pollution of air and water if atmospheric emissions and liquid and solid wastes are not disposed of properly.

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* Alloy contained 3.5 percent zinc which accounts in part for the low furnace emissions factor.

Population of Secondary Brass and Bronze Processors

(1) Barth Smelting Corporation
99-129 Chapel Street
Newark, New Jersey
Telephone: (201) MA2-4903

(2) Bridgeport Brass Company
Division of National Distillers
and Chemicals Corporation
30 Grand Street
Bridgeport, Connecticut 06602

(3) Bristol Brass Corporation
999 Broad Street
Bristol, Connecticut
Telephone: 582-3161

(4) W. J. Bullock, Inc.
Post Office Box 539
Fairfield, Alabama

(5) The Bunting Brass and Bronze Co.
715 Spencer Street
Toledo, Ohio 43601
Telephone: (419) EV2-3451

(6) Cerro Corporate Brass Company
Division of Cerro Corporation
16600 St. Clair Avenue
Cleveland, Ohio 44110
Telephone: (216) 481-3000

(7) Colonial Metals Company
Columbia, Pennsylvania
Telephone: (717) 684-2311

(8) Federated Metals
Division of American Smelting
and Refining Company
12 Pine Street
New York, New York

(9) Franklin Smelting and Refining
Company
Castor Avenue
East of Richmond
Philadelphia, Pennsylvania 19140
Telephone: (215) NE4-2231

(10) Freedman Metal Company
310 McGinnis Boulevard
Brooklyn, New York 11222
Telephone: EV9-4131

(11) General Copper and Brass
Company
Post Office Box 5353-D
Philadelphia, Pennsylvania
Telephone: SA6-7111 (215)

(12) Benjamin Harris & Company
Eleventh and State Streets
Chicago Heights, Illinois

(13) Henning Brothers & Smith,
Inc.
91-115 Scott Avenue
Brooklyn, New York

(14) K. Hettleman & Sons
Division of Minerals &
Chemicals
Phillip Corporation
Ninth Street and Patapsco Ave.
Baltimore, Maryland 21225
Telephone: (301) 355-0770

(15) Holtzman Metal Company
5223 McKissock Avenue
St. Louis, Missouri 63147
Telephone: (314) CH1-3820

(16) H. Kramer & Company
1339-15 West 21st Street
Chicago, Illinois 60608
Telephone: CA6-6600

(17) Lewistown Smelting and
Refining Inc.
Post Office Box 708
Lewistown, Pennsylvania
Telephone: (713) 543-5631

(18) Magnolia Metal Company, Inc.
Magnolia Park
Auburn, Nebraska
Telephone: (412) 274-3152

(19) Metal Bank of America, Inc.
6801 State Road
Philadelphia, Pennsylvania 19135
Telephone: (215) 332-6600

(20) North American Smelting Company
Post Office Box 1952
Wilmington, Delaware
Telephone: OL4-9901

(21) Northwestern Metal Company
North 27th Street
Lincoln, Nebraska
Telephone: 434-6341

(22) Phelps Dodge Refining Corporation
300 Park Avenue
New York, New York
Telephone: 751-3200

(23) Riverside Alloy Metal Division
H. J. Porter Company, Inc.
309 Porter Building
Pittsburgh, Pennsylvania 15219
Telephone: (412) 391-1800

(24) Rochester Smelting and Refining Company, Inc.
Post Office Box 547
Rochester, New York

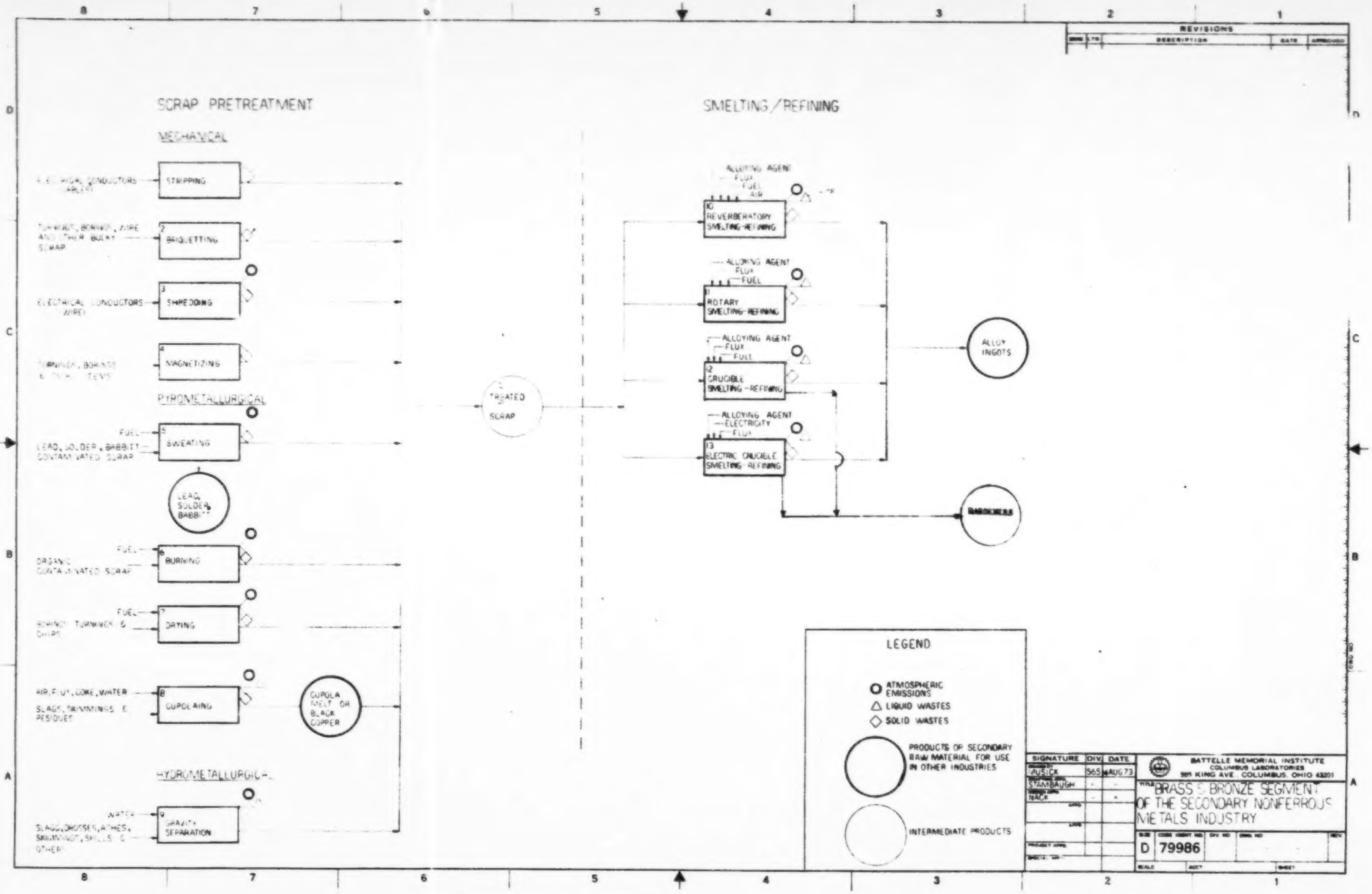
(25) Roessing Bronze Company
320 Barbour
Pittsburgh, Pennsylvania

(26) The George Sall Metals Company, Inc.
2255 E. Butler Street
Philadelphia, Pennsylvania 19137
Telephone: (215) PI3-3900

(27) SIPI Metals Corporation
1722 N. Elston Avenue
Chicago, Illinois

(28) Solken-Galamba Corporation
Second and Riverview Streets
Kansas City, Kansas 66118
Telephone: (913) MA1-4100

(29) U. S. Metal Products Company
Post Office Box 1067
Erie, Pennsylvania 16512
Telephone: (814) 838-2051


SCRAP PRETREATMENT
MECHANICAL
ELECTRICAL CONDUCTORS (CABLES)
STRIPPING
TURNINGS, BORINGS, WIRE AND OTHER BULKY SCRAP
2 BRIQUETTING
ELECTRICAL CONDUCTORS (WIRE)
3 SHREDDING
TURNINGS, BORINGS & OTHER ITEMS
4 MAGNETIZING
PYROMETALLURGICAL
FUEL
LEAD, SOLDER, BABBITT CONTAMINATED SCRAP
5 SWEATING
LEAD, SOLDER, BABBITT
FUEL
ORGANIC CONTAMINATED SCRAP
6 BURNING
FUEL
BORINGS, TURNINGS & CHIPS
7 DRYING
AIR, FLUX, COKE, WATER
SLAGS, SKIMMINGS & RESIDUES
8 CUPOLAING
CUPOLA MELT OR BLACK COPPER
HYDROMETALLURGICAL
WATER
SLAGS, DROSSES, ASHES, SKIMMINGS, SPILLS & OTHER
9 GRAVITY SEPARATION
TREATED SCRAP
SMELTING/REFINING
ALLOYING AGENT
FLUX
FUEL
AIR
10 REVERBERATORY SMELTING-REFINING
ALLOYING AGENT
FLUX
FUEL
11 ROTARY SMELTING-REFINING
ALLOYING AGENT
FLUX
FUEL
12 CRUCIBLE SMELTING-REFINING
ALLOYING AGENT
ELECTRICITY
FLUX
13 ELECTRIC CRUCIBLE SMELTING-REFINING
ALLOY INGOTS
[redacted]
LEGEND
○ ATMOSPHERIC EMISSIONS
△ LIQUID WASTES
◇ SOLID WASTES
PRODUCTS OF SECONDARY RAW MATERIAL FOR USE IN OTHER INDUSTRIES
INTERMEDIATE PRODUCTS
REVISIONS
DESCRIPTION
DATE
APPROVED
SIGNATURE
DIV.
DATE
MUSICK
565
AUG 73
STAMBAUGH
NACK
BATTELLE MEMORIAL INSTITUTE
COLUMBUS LABORATORIES
505 KING AVE., COLUMBUS, OHIO 43201
BRASS & BRONZE SEGMENT OF THE SECONDARY NONFERROUS METALS INDUSTRY
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PROCESSING DESCRIPTION OF THE CADMIUM SEGMENT OF THE SECONDARY NONFERROUS METALS INDUSTRY

Cadmium is a byproduct of the primary zinc system. During 1971, total U.S. cadmium production was 7.9 million pounds of which the secondary cadmium segment production was 400,000 pounds or about 5 percent of the total.*

Cadmium is a poisonous metal. Ingestion as fumes or in other forms is known to cause the painful "itai-itai" disease. Hence, it is generally considered both necessary and safe to use a replacement metal that provides all the excellent properties of cadmium without its toxicity. Zinc is a possible replacement metal.

Raw Materials

Raw material is available both as old and new scrap. Examples of old scrap are: cadmium plated parts from junked automobiles, nickel-cadmium batteries, cadmium coated electrical contact points, and used cadmium alloys. New scrap, which constitutes only a small percentage of the total, consists of factory rejects from manufacturing of bearings etc., Ni-Cd battery rejects, and scrap from plating (electrodeposition) cells, and scrap solder used to solder aluminum.

In the United States, cadmium is not recovered from junked automobile parts because of economics. Also, used nuclear reactor control rods (containing 80 percent cadmium and 20 percent silver and indium) are not processed by the secondary cadmium industry. Instead these rods are sent to fuel processors (e.g., Mallinckrodt Chemical Works, St. Louis, Missouri).

Products

Products of the cadmium segment are as follows:

(1) Recast cadmium metal (sticks and balls)

(2) Recast cadmium alloys.

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* U. S. Bureau of Mines

Process Description

The three manufacturing operations employed in scrap processing are scrap pretreatment, smelting/refining, and casting--as described below and as shown on the flowsheet of this segment. Of these, the major operation--smelting/refining--involves pyrometallurgy.

Scrap Pretreatment Operation

The only process in this operation is the vapor degreasing of alloy scrap as noted by Process 1.

Vapor Degreasing Process (1). This process removes oil and grease adhering to the scrap alloys.

The process steps are: (1) heating solvent to generate vapors (perchloroethylene), (2) circulating solvent vapors through the scrap in a pot, and (3) condensing solvent for reuse.

Heat energy is the main requirement of this process.

The major waste generated is the liquid waste--grease/oil residue from the solvent regeneration pot. The quantities of this waste are very small and are usually either incinerated at the municipal incinerator or dumped into sewer lines. Other waste generated is atmospheric emission composed of organic vapors.

The potential for pollution from this process is not significant, and is regulated in many states.

Smelting/Refining Operation

Two processes--melting or retorting--are used to recover cadmium from scrap.

Alloy Smelting/Refining Process (2). This process purifies the pretreated alloy scrap.

The process steps involved are: (1) heating the alloy scrap, (2) adding the flux, (3) skimming the slag, and (4) pouring the molten metal into molds for casting.

Heat energy is utilized in the process.

Wastes generated are atmospheric emissions containing metal fumes and solid wastes consisting of slag. The fumes are not significant to cause any pollution. The slag is recycled and ultimately disposed of in a landfill. Thus, the process has a low pollution potential.

Retort Smelting/Refining Process (3). This process recovers pure cadmium by distilling cadmium alloys.

The process steps are: (1) charging the retort, (2) melting the charge, (3) vaporizing the cadmium, (4) condensing the cadmium, (5) pouring the molten metal, (6) casting the ingots, and (7) discharging retort residue for shipping to residue processors.

Heat energy is utilized in the process. The potential pollutant generated by this process is atmospheric emissions containing cadmium fumes.

If properly controlled, this process has little potential for producing serious pollution problems.

Melting Process (4). This process purifies the scrap cadmium metal collected from electrodeposition cells as sticks and rods. These rods and sticks are usually contaminated with acid salts or mixed with zinc occasionally.

The process steps are: (1) charging scrap to pot, (2) melting the charge, (3) adding the flux, (4) chlorinating when required for zinc removal, (5) skimming the slag, (6) pouring into molds, and (7) casting the ingots.

The process utilizes heat energy.

Wastes generated in the process are: (1) atmospheric emissions containing cadmium fume, zinc chloride dust when dezincing operation is done, (2) solid waste consisting of slag, and (3) liquid waste composed of cooling water which may be recycled. The zinc chloride dust is collected with a baghouse. Slag generated is about 2000 pounds per year in a plant producing 200,000 pounds of cadmium per year. The slag which contains some cadmium is disposed of in a landfill.

Thus, this process has the potential for the production of pollution problems.

Casting Operation

This is a simple operation and consists of one process step.

Casting Process (5). The molten alloy and the molten metal from the retorting and melting processes are cast into required shapes by this process. The processing steps consist of pouring the molten material into molds and casting with water cooling.

Electrical energy is used to circulate cooling water and auxiliary equipment.

No wastes are generated in the process. The process has no pollution potential.

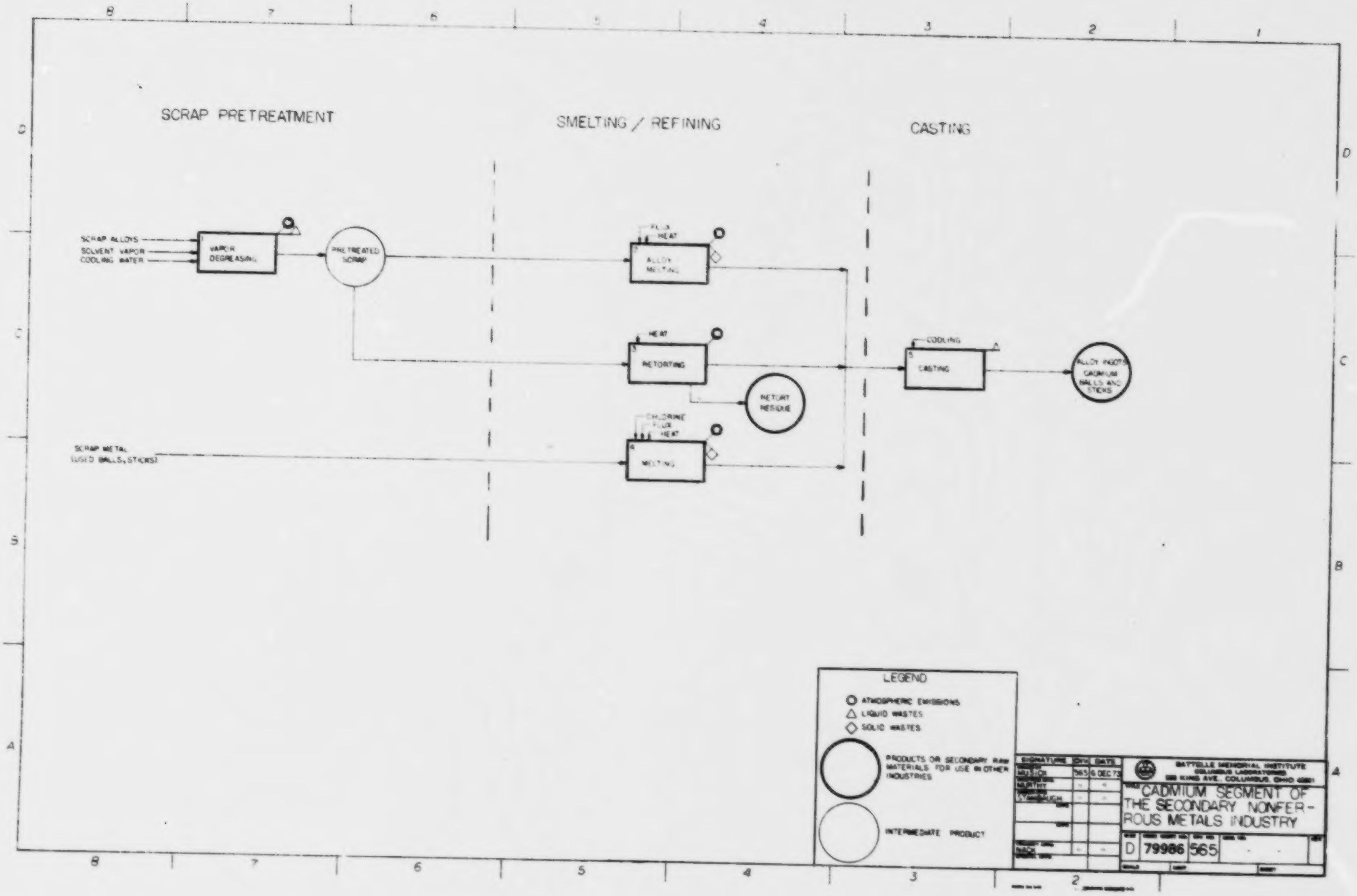
Population of Secondary Cadmium Processors

(1) Belmont Smelting & Refining Works
320 Belmont Avenue
Brooklyn, New York

(2) Joseph Behr & Sons, Inc.
1100 Seminary Street
Rockford, Illinois

(3) United Refining and Smelting Company
3700-20 N. Runge Avenue
Franklin Park, Illinois 60131

(4) Wolverine Metal Company
6500 E. Robinwood Street
Detroit, Michigan


SCRAP PRETREATMENT
SMELTING / REFINING
CASTING
SCRAP ALLOYS
SOLVENT VAPOR
COOLING WATER
1 VAPOR DEGREASING
PRETREATED SCRAP
FLUX
HEAT
2 ALLOY MELTING
HEAT
3 RETORTING
RETORT RESIDUE
CHLORINE
FLUX
HEAT
4 MELTING
SCRAP METAL (USED BALLS, STICKS)
COOLING
5 CASTING
ALLOY INGOTS CADMIUM BALLS AND STICKS
LEGEND
ATMOSPHERIC EMISSIONS
LIQUID WASTES
SOLID WASTES
PRODUCTS OR SECONDARY RAW MATERIALS FOR USE IN OTHER INDUSTRIES
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BATTELLE MEMORIAL INSTITUTE
COLUMBUS LABORATORIES
505 KING AVE., COLUMBUS, OHIO 43201
CADMIUM SEGMENT OF THE SECONDARY NONFERROUS METALS INDUSTRY
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PROCESS DESCRIPTION OF THE COBALT SEGMENT OF THE SECONDARY NONFERROUS METALS INDUSTRY

The volume of scrap available to the cobalt segment of the secondary nonferrous metals industry is estimated at two million pounds annually. The majority of this is recovered as cobalt-base or nickel-base alloy in the United States. Some of the refined high grade cobalt scrap is exported to Japan for recovery of pure metal. Approximately 5 to 10 percent of the scrap cobalt is used in the production of chemicals.

Emissions from the cobalt segment include (1) water wastes from vapor degreasing, pickling and vacuum melting, and (2) minor quantities of wastes to the ambient air and land from other process steps. Generally, these wastes are effectively controlled and therefore their potential for pollution is minimized. However, if the control methods are rendered ineffective, a moderate potential for pollution of mainly the waterways exists.

Raw Materials

Raw materials consist of cobalt bearing superalloy grindings and turnings and scrap superalloys (stellite, etc.) from jet engine components. The total scrap available can be classified into cobalt-base superalloy scrap containing 50 to 60 percent cobalt and nickel-base scrap consisting of 10 to 20 percent cobalt. A quantitative breakdown of the scrap into these categories is not available because of the lack of information, published or otherwise.

Products

Products from the secondary cobalt industry are as follows:

(1) Pig alloys (stellites, etc.)

(2) Refinery grade cobalt scrap.

Process Description

Processing of scrap cobalt alloys involves three major operations--scrap pretreatment, smelting, and casting/refining. These operations are shown in the attached flowsheet for this segment.

Scrap Pretreatment Operation

A complex series of processes are involved in this operation. Some companies specialize in these processes and produce a clean scrap as their product for sale to smelting facilities.

The four processes (Process 1 through Process 4) employed under this operation are described below.

Hand Sorting Process (1). This process identifies the scrap components and separates them into cobalt-base, nickel-base and nonprocessable components. The hand sorting operation is also aided by identifying the source of scrap and storing them in different lots to avoid mixing.

The processing steps are: (1) spreading the dirty scrap on the floor, and (2) visually identifying and segregating the scrap.

Human labor is the only requirement of this process.

Waste produced is a minor amount of dust which is collected as sweepings and disposed of in trash cans and ultimately in a landfill.

The process has no potential for pollution. The cobalt free scrap collected in the process is sent to other processing facilities.

Vapor Degreasing Process (2). This process removes the oil and grease from the scrap by using hot vapors of perchloroethylene.

The processing steps are: (1) charging dirty scrap to degreasing unit, (2) heating to generate and circulate hot solvent vapor, and (3) discharging the degreased scrap to the blasting box.

Heat energy is the main energy requirement of the process.

Waste emissions include minor amounts of solvent vapor to the atmosphere and grease and oil wastes to be incinerated or disposed of in sewers.

Since the process is a closed loop operation, the only significant waste with a potential for pollution is the grease and oil from the solvent recovery unit.

Blasting Process (3). This process cleans the surface of the scrap material of all extraneous dirt, oxides, and rust.

The process steps are: (1) blast the scrap either batchwise or continuously with grit, and (2) discharge the clean scrap.

The process requires electrical energy to obtain compressed air used in the blasting equipment.

Since the process is a closed loop operation, no significant wastes are generated. Hence the process has no potential for pollution.

Pickling and Chemical Treatment Process (4). Because the alloy produced as the final product of this segment has to be free of all impurities, the pickling process is utilized to clean the scrap of all residual oxide coatings. The chemical treatment operation is a trade secret and is known to remove lead from the scrap.

The process steps are: (1) treating the scrap with a mixture of acids to remove rust and oxides, (2) treating with a chemical to remove lead, and (3) washing the scrap with water.

The process requires electrical energy to drive pumps and other auxiliary equipment.

Waste discharges include (1) small amount of acid fumes and (2) acidic wastewater containing metallic impurities.

The acidic wastewater is neutralized before discharge to the waterways or sewer and hence has a reduced pollution potential. The acid fumes are usually not substantial to create serious ambient air pollution problems.

Smelting/Refining Operation

The treated scrap is virtually free of all impurities except for some dissolved gases which are removed by smelting/refining. Usually this operation is carried out in an electric arc vacuum furnace or a vacuum induction furnace.

Vacuum Melting Process (5). This process refines the scrap by removing volatile impurities under the influence of both heat and vacuum.

The process steps include: (1) charge scrap to the vacuum furnace, (2) evacuate the system, (3) melt the scrap by electric arc or induction, and (4) discharge the molten alloy into molds.

Large amounts of electrical energy are used both to create vacuum and heat the charge.

No significant wastes are produced. The vacuum pump discharge is contaminated with traces of gaseous wastes too insignificant to constitute any pollution. Vaporized heavy metals and other potential pollutants are trapped by the vacuum pump.

Casting Operation

This is the final operation of the secondary cobalt industry. The castings produced by this operation are used as pig alloys or if the quality of the alloys produced is refinery grade cobalt alloy, it may be shipped to a cobalt metal recovery facility.

Casting Process (6). This process produces castings of pig alloy from the molten charge obtained in vacuum melting.

The process steps are: (1) pouring the molten metal into molds and (2) casting the ingots.

Energy requirements of this process are not significant.

No wastes are produced in the process.

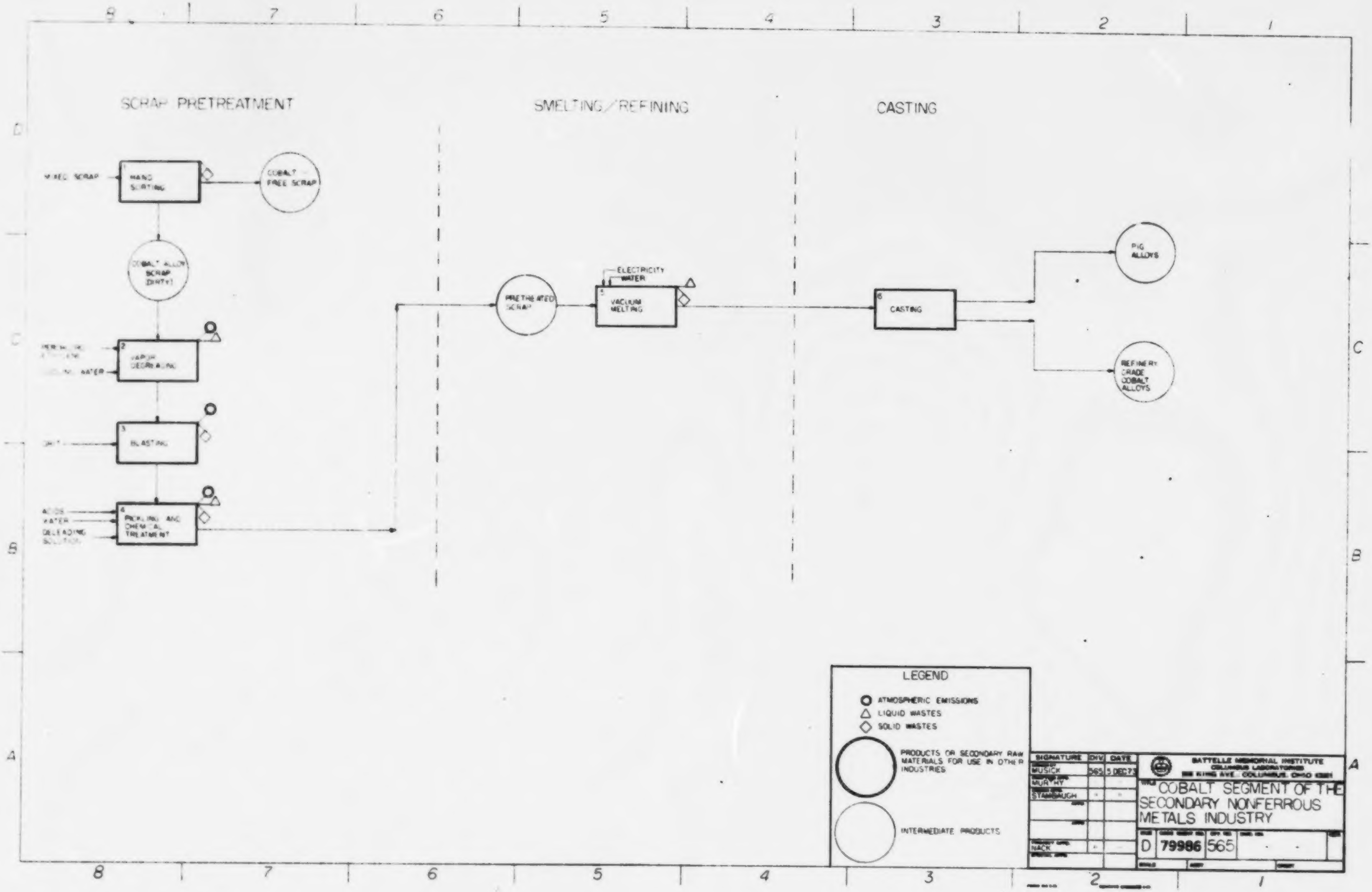
Population of Secondary Cobalt Processors

Alloy Metal Products, Inc.
626 Schmidt Road
Davenport, Iowa 52808
Telephone: (319) 324-3511

Max Zuckerman and Sons
Music Fair Road
Owings Mills, Maryland 21117
Telephone: (301) 484-0400

Pfizer Metals and Composite Products
235 E. 42nd Street
New York, New York 10017
(Processing only inhouse scrap)

Union Carbide Stellite Division
Kokomo, Indiana
Telephone: (317) 457-8411


SCRAP PRETREATMENT
SMELTING/REFINING
CASTING
MIXED SCRAP
1 HAND SORTING
COBALT - FREE SCRAP
COBALT ALLOY SCRAP (DIRTY)
PERCHLORO-ETHYLENE
COOLING WATER
2 VAPOR DEGREASING
GRIT
3 BLASTING
ACIDS
WATER
DELEADING SOLUTION
4 PICKLING AND CHEMICAL TREATMENT
PRETREATED SCRAP
ELECTRICITY
WATER
5 VACUUM MELTING
6 CASTING
PIG ALLOYS
REFINERY GRADE COBALT ALLOYS
LEGEND
ATMOSPHERIC EMISSIONS
LIQUID WASTES
SOLID WASTES
PRODUCTS OR SECONDARY RAW MATERIALS FOR USE IN OTHER INDUSTRIES
INTERMEDIATE PRODUCTS
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MURPHY
STAMBAUGH
NACK
BATTELLE MEMORIAL INSTITUTE
COLUMBUS LABORATORIES
505 KING AVE. COLUMBUS, OHIO 43201
COBALT SEGMENT OF THE SECONDARY NONFERROUS METALS INDUSTRY
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PROCESS DESCRIPTION OF THE COPPER SEGMENT OF SECONDARY NONFERROUS METALS INDUSTRY

Tonnage-wise, the copper segment (which produces refined copper) constitutes one of the major segments of the secondary nonferrous metals industry. Based on 1972 data(1), 1,210,070 tons of copper were recovered from scrap. Of this production, 280,730 tons were recovered by this segment and 571,095 tons were recovered by the brass and bronze segment. An additional 381,790 tons were recovered by the primary nonferrous metals industry. Emissions from the copper segment of the secondary industry include: gases and particulate materials which are emitted to the atmosphere, liquid wastes emitted to the water system, and solid wastes emitted to the land.

Raw Materials

Sources of raw materials to this industry include both new and old scrap. New scrap, which accounted for approximately 21 percent of the copper recovered from the scrap in 1972, refers to scrap produced in the manufacturing process by a fabricator of a finished product. Old scrap, comprising obsolete, worn out, or damaged articles, accounts for approximately 69 percent of the copper recovered by the copper segment in the U. S.

Segregating scrap according to classification standards is one of the most important steps in the recovery of secondary metals. Currently, copper-bearing scrap is classified into 54 types(2) as shown in Table III.

Copper scrap as received generally contains metallic and nonmetallic impurities. Included among these are: lead, zinc, tin, antimony, iron, manganese, nickel, chromium, precious metals, and organic compounds such as plastics, oils, and greases. These impurities, which are removed during the recovery of copper, constitute major sources of emissions to the environment, if not collected and disposed of by an acceptable method or recovered as by-products.

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(1) "Copper industry in January 1973", Mineral Industry Surveys, U. S. Dept. of the Interior, Bureau of Mines, Washington, D. C.

(2) Circular NF-58, National Association of Waste Materials Dealers, Inc.

Products

Products from the copper segment of the secondary nonferrous metals industry include:

(1) Babbit, lead, and solder recovered from the sweating process. This mixture of materials may be made into white-metal alloys, used for lead and tin additions to copper base alloys, or sold as produced to a refiner.
(2) Copper powder
(3) Copper shot
(4) Fire-refined copper
(5) Electrolytic-refined copper
(6) Oxygen-free high conductivity copper (O.F.H.C.)*

Process Description

The recovery of copper from scrap involves three manufacturing operations: scrap pretreatment, smelting, and refining/casting. These operations and the individual processes under each operation are shown on the flowsheet entitled "Copper Segment of the Secondary Nonferrous Metals Industry".

Scrap Pretreatment Operation

Copper scrap is pretreated prior to smelting to remove some of the metallic and nonmetallic impurities or contaminants and to physically prepare the material for further processing. Three types of processing--mechanical, pyrometallurgical, and hydrometallurgical--are used. The pretreatment process varies according to the type of scrap. The individual pretreatment processes are numbers 1 through 14 on the segment flowsheet.

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* O.F.H.C. is a trade name of the U. S. Metals Refining Company.

Stripping Process (1). Insulation and lead sheathing are removed from electrical conductors by special stripping machines or by hand.

Energy demand is that needed to drive the equipment.

The process produces quantities of solid wastes. These wastes include lead and insulation. The lead is probably sold to a secondary lead smelter, whereas the insulation may be sent to a landfill or incinerator.

The process has little potential for production of serious pollution.

Briquetting Process (2). Wire, thin plate, wire screen, and other bulky scrap are pressed into briquettes, bales, or bundles by hydraulic presses. In this form, the scrap is easier to handle, store, and load into the furnace.

Energy required is that necessary to drive the presses.

The process produces essentially no wastes or emissions.

The process has no potential for production of pollution problems.

Shredding Process (3). Large items are reduced in size by pneumatic cutters, electric shearing machines, or manual sledging. The smaller pieces are easier to handle.

Energy demand is limited to that needed to drive the equipment.

The process may produce a small quantity of atmospheric emissions consisting of dusts with an approximate composition of the scrap. Collection of these dusts may be via a baghouse. Most likely, the emissions are not controlled.

The process has essentially no potential for production of pollution problems.

Crushing Process (4). Brittle spongy turnings, borings, and long chips are densified by the crushing process. The process steps are: (a) crushing in hammermills or ballmills to reduce bulk, and (b) running over a magnetic separator to remove tramp iron.

Energy demand is that required to drive the equipment.

The process produces small quantities of atmospheric emissions consisting of dust particles composed of dirt, organic compounds from the scrap, heavy metals, and solid wastes. Most likely, the area may be hooded to carry the dust away from the vicinity of the crushing.

The process has little or no potential for causing serious pollution problems.

Grinding Process (5). Prills or metallics are seperated from the gangue in slags, drosses, skimmings, foundry ashes, spills, and sweepings by the grinding process. The process steps are: (a) grinding, (b) screening, and (c) gravity separation.

Energy required is that to drive the equipment.

The process produces atmospheric emissions, liquid wastes, and solid wastes. The atmospheric emissions are dusts from the grinding and screening steps. These dusts may contain, in addition to fluxing materials and dirt, small quantities of heavy metals.

The liquid wastes containing both dissolved and suspended solids are generated in the gravity separation step. The solid wastes are generated during the screening step.

As significant quantities of atmospheric emissions, liquid wastes, and solid wastes are generated by the grinding process, the process has a potential for the production of pollution problems.

Muffle/Kiln Burning/Drying Process (6). Much of the scrap contains oil, grease, cutting fluids, insulation, and moisture. These components may be removed prior to smelting by the muffle/kiln/burning/drying process. The process steps are: (a) charging of the scrap to the muffle or kiln, and (b) heating to remove the organic contaminants and moisture, afterwhich the treated scrap is removed for further processing.

Energy required for this process is from gas or fuel oil to heat the furnace and electricity to drive the equipment.

The process produces significant quantities of atmospheric emissions. These emissions consist of both gases and particulate matter. The gaseous emissions are composed of the gases from combustion of the fuel and the organic contaminants. Depending on the organic contaminants, the gases may contain such materials as the chlorides, sulfur oxides, fluorides, and hydrocarbons. The particulate matter (fume and dust) is composed of a variety of heavy metals depending on the composition of scrap. Examples of heavy metals which may be found in the particulate matter are copper, zinc, tin, and lead.

Emissions data are not available for the burning/drying of all types of scrap. However, from burning of insulated wire, particulate emissions are estimated at 275 lb per ton of wire processed(3) or an annual emissions total of 41,000 tons based on treating 300,000 tons of insulated wire.

A variety of methods may be employed to control the atmospheric emissions. Included in the list are afterburners to destroy the hydrocarbons and other organic materials, wet scrubbers to remove the particulate matter and toxic gases, and baghouses to remove the particulates.

In view of the toxic and hazardous nature of the atmospheric emissions, this process could be a source of serious pollution problems if the emissions are not controlled.

Sloping Hearth Sweating Process (7). Scrap such as journal bearings, radiators, and lead-sheathed cable contains lead, solder, or babbitt which would contaminate the melt. These contaminants are removed by the sloping hearth sweating process. The process steps are: (a) charging the preheated furnace with scrap, (b) melting the low-melting constituents, (c) raking the sweated scrap over the hearth to remove all of the low-melting alloys, (d) collecting the solder, lead, or babbitt in a collecting pit, and (e) removing the sweated scrap for further processing.

Energy for this process is from gas to fire the furnace.

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(3) Vandegrift, A. E., et al., Particulate Pollutant System Study, Handbook of Emissions Properties, Midwest Research Institute, Kansas City, Missouri, Volume III, p 406 (May 1, 1971).

In addition to the lead, solder, or babbitt which are recovered for subsequent use or sale, the process produces atmospheric emissions. These emissions are composed of gases and fumes. The gases contain the products from combustion of the fuel and any organic matter present in the scrap. Particulate matter is composed of such heavy metals as lead, tin, antimony, and copper, and organic materials such as soot.

Emissions data are not available for the sweating of the various types of scrap. However, the sweating of radiators results in the evolution of 15 lb of particulate matter per ton of scrap.

Emissions may be controlled by baghouses, wet scrubbers, and electrostatic precipitators.

Due to the hazardous nature of some of the pollutants and the quantity emitted, this process has a potential for the production of serious pollution problems.

Reverberatory Sweating Process (8). For removal of solder from scrap which is difficult to sweat, i.e., the solder remains in seams and folds when melted, the reverberatory sweating process may be employed. For this process a reverberatory furnace with a shaking grate is used. The molten solder removed from the items by a shaking motion falls to the floor and flows to the collecting sump. The process steps are: (a) charging the furnace, (b) heating the scrap to melt the low-melting components, (c) shaking to remove the low-melting components, and (d) collecting the low-melting material. The sweated scrap is subsequently removed for further processing.

Energy demand is from the fuel oil or gas to heat the direct-fired reverberatory and electricity to drive the equipment.

Waste materials produced by this process are atmospheric emissions consisting of gases and particulate matter. Composition of these emissions is similar to those from the sloping hearth smelting process. In fact, if the same type of scrap were sweated by both processes, the emission would be essentially identical with the possible exception that the emissions from the reverberatory sweating process may contain some dust resulting from shaking action. This dust is carried from the furnace by entrainment in the combustion gases.

Particulate emission factor for reverberatory sweating process is estimated at 15 lb/ton of radiators. The factor may be lower or higher for other types of scrap.

Emissions are controlled with the same equipment as is used for other sweating processes.

Atmospheric emissions produced by this process could cause pollution problems.

Pot Sweating Process (9). Removal of low-melting constituents from copper scrap is achieved by the pot sweating process. The process steps are: (a) dipping the scrap into a pot of molten alloy, (b) melting the low-melting constituents, and (c) removing the sweated scrap from the pot.

Energy required is fuel--gas or oil--necessary to keep the pot of alloy molten.

Potential pollutants generated by this process are atmospheric emissions containing fumes and possibly some gases if the scrap to be sweated contains any organic matter. Composition of emissions and emission factors should be comparable to those from other sweating processes.

The process has the potential for producing pollution problems, as well as hazards to the operators of the equipment.

Tunnel Sweating Process (10). This process is used by some smelters to sweat copper scrap. The process steps are: (a) load scrap placed in trays or on racks onto a continuous conveyor passing through the tunnel furnace, (b) remove the major portion of the low-melting constituents by passing the scrap through a heated tunnel furnace, and (c) dump hot partially sweated scrap onto tilted screen to remove remaining low-melting constituents. The molten low-melting constituents are collected in a floor sump.

Energy required is from oil or gas to heat the scrap and electricity to drive the equipment.

This process produces atmospheric emissions composed of gases (combustion gases from the fuel and gases from burning or volatilization of organic contaminants in the scrap), and particulate matter (fumes and possibly some dust from dropping of the partially sweated scrap onto the screen). The individual components in the emissions will be the same as those in emissions from other similar processes.

Particulate emission factor may be somewhat higher for this process (>15 lb/ton of scrap sweated) as the partially sweated scrap is exposed to the atmosphere while hot. This results in rapid oxidation of molten metal and subsequent volatilization of the oxides as fumes.

The process produces atmospheric emissions which can cause pollution problems.

Ammonium Carbonate Leaching Process (11). The copper values are leached from copper scrap by the ammonium carbonate leaching process.(4,5) The process steps are: (a) heating copper scrap in an ammonium carbonate solution while sparging the solution with air, (b) separating the crude copper ammonium carbonate solution from the leach residue, and (c) purifying the clarified copper solution. Copper values are then recovered from this intermediate product by the steam distillation process (12) or by the hydrothermal hydrogen reduction process (13).

The energy required for this process is that necessary to heat the solution and to drive the equipment.

The potential environmental pollutants generated by this process are atmospheric emissions, liquid wastes, and solid wastes. The atmospheric emissions are gases emitted from the leaching of the copper scrap with ammonium carbonate in the preparation of the crude copper ammonium carbonate solution. These emissions contain ammonia,

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(4) Kunda, W., et al., "Production of Copper from the Amine System", presented at Extractive Metallurgy Division Symposium on Copper Metallurgy, Denver, Colorado, February 15-19 (1970).

(5) Ryan, V. H., et al., Production of Copper Powder: AICE, National Meetings, Washington, D. C., March 9, 1954.

water vapor, carbon dioxide, nitrogen, and excess air. Before being emitted to the atmosphere, the gases are cleaned via a wet scrubber which removes the ammonia and carbon dioxide.

Solid wastes generated by the process are the leach residues and residues from the various stages of solution purification.

Essentially the only liquid wastes generated are those adsorbed on the surface of the discarded residues. Other liquid effluents generated are recycled to the process.

Thus, this process has essentially no potential for the production of atmospheric pollution problems. The only atmospheric emission generated is nitrogen enriched air from the leaching operation. However, there is a potential for water pollution resulting from disposal of the leach residues from the ammonium carbonate leaching of the copper scrap and the disposal of purification residues. Pollution problems resulting from disposal of liquid wastes are negligible as essentially all of the liquid effluents are recycled.

Steam Distillation Process (12). Copper oxide is precipitated from the copper solution prepared from the ammonium carbonate leaching process by the steam distillation process. The process steps are: (a) heating the copper solution to precipitate the copper, (b) separating copper values from slurry, (c) drying the precipitated copper oxide, and (d) recycling the aqueous effluent to the ammonium carbonate leaching process to prepare fresh copper. The copper oxide is an intermediate product for the production of copper by such processes as (15) and (24). Step (a) is conducted at atmospheric pressure (boiling) or under pressure.

The energy requirement is that to produce the steam to heat the calciner.

The process produces some atmospheric emissions from the copper ammonium carbonate decomposition step (Step a), and during drying of the copper oxide, and possibly some liquid wastes. The gaseous emissions from Step (a) are composed of essentially water vapor, ammonia, and carbon dioxide. These gases may contain a trace of copper carried from the system by entrainment in the gaseous emissions. Those emissions from drying of the copper oxide contain gaseous emissions composed of water vapor, carbon dioxide, and possibly some ammonia, and particulate emissions consisting of essentially copper along with trace quantities of other metals found in the copper oxide as impurities.

Control of the atmospheric emissions should be possible by using a wet scrubber for controlling those from Step (a), and by using a wet scrubber or baghouse to control those from the calciner.

The liquid wastes are dilute ammonium carbonate solutions from washing the precipitated copper oxide. These contain, in addition to ammonium carbonate, copper compounds along with trace quantities of impurities associated with the copper. In most cases, these wastes can be recycled.

Because of the small amount of wastes produced by this process, it is expected that pollution problems associated with the wastes are minor.

Hydrothermal Hydrogen Reduction Process (13). The copper value is precipitated as metallic copper from the ammonium carbonate leaching process by the hydrothermal hydrogen reduction process. The process includes the following process steps: (a) heating the copper solution in an autoclave with hydrogen at an elevated temperature and pressure to precipitate the copper, (b) removing the stripped liquor from the metallic copper, (c) washing the copper free of adsorbed liquor, (d) drying and sintering the copper powder under a hydrogen atmosphere, (e) pulverizing the sinter, and (f) screening the powder.(6) The reduction of the copper solution is conducted at approximately 325 F and 500 psig of hydrogen. The stripped liquor is recycled to produce more copper solution by the ammonium carbonate leaching process.

The energy requirement is that needed to heat the copper solution in the reduction step, to dry and sinter the copper product, and to drive the pulverizing and screening equipment.

Atmospheric emissions and possibly liquid emissions are generated by this process. Sources of atmospheric emissions are (1) drying and sintering of the copper powder, (2) pulverizing and screening of the copper sinter, and (3) reduction of the copper solution. The emissions from drying and sintering of copper powder contain water vapor, hydrogen, ammonia, and carbon dioxide as gases, and possibly particulates of copper powder or copper oxide. Those from the pulverizing and screening of the copper sinter contain particulates of copper. The gas in these emissions is entrained air. Hydrogen and water vapor are emitted from reduction of the copper solution.

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(6) Kunda, W., et al., "Production of Copper From Amine Carbonate System", 1970 Extractive Metallurgy Division Symposium on Copper Metallurgy, Denver, Colorado, pp 40-43 (1970).

Liquid wastes are ammonium carbonate solutions containing such metal value as copper, nickel, lead, and zinc. Normally, these are regenerated and recycled. If the ammonia and ammonium carbonate contents are low, the solutions may be discarded. No solid wastes are produced by this process.

Thus, the process produces emissions and wastes which could cause pollution problems. However, the quantity of emissions is expected to be low; therefore, pollution problems associated with this process are expected to be minor.

Sulfuric Acid Leaching Process (14). Copper values are extracted from scrap copper as copper sulfate by this process. The process steps are as follows: (a) digesting copper scrap in hot aerated sulfuric acid solution to convert the copper values to copper sulfate, (b) separating the soluble copper sulfate from the undissolved portion of the scrap by filtration, and (c) purification of the copper sulfate solution. This intermediate product--aqueous copper sulfate solution--is a source of copper for the electrowinning process.

The energy requirement is that to heat the digester solution and to operate the auxiliary equipment.

The wastes produced by this process are atmospheric emissions and solid waste. The source of atmospheric emissions is the digester. These consist of air containing fine droplets of the pregnant leach liquor. Most are equipped with demisters to reduce the emissions to the environment.

The undissolved portion of the scrap and residues formed during the purification step are the sources of solid wastes. These are, most likely, disposed of via landfill. However, care must be taken to prevent contamination of the water by leachate from the landfill. A portion of the wastes may be reclaimed.

screening of the copper sinter, and (3) reduction of the copper solution. The emissions from drying and sintering of copper powder contain water vapor, hydrogen, ammonia, and carbon dioxide as gases, and possibly particulates of copper powder or copper oxide. Those from the pulverizing and screening of the copper sinter contain particulates of copper. The gas in these emissions is entrained air. Hydrogen and water vapor are emitted from reduction of the copper solution.

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The undissolved portion of the scrap and residues formed during the purification step are the sources of solid wastes. These are, most likely, disposed of via landfill. However, care must be taken to prevent contamination of the water by leachate from the landfill. A portion of the wastes may be reclaimed.

This process produces essentially no atmospheric emissions and, thus, does not pose an atmospheric pollution problem. However, solid wastes disposal may result in a water pollution problem.

Smelting Operation

The scrap pretreatment operation achieves a partial purification or densification of copper-bearing scrap. Further purification is achieved by the smelting operation as outlined in the segment flowsheet by Processes 15 through 17. Via this operation, additional metallic and nonmetallic impurities are removed from the copper scrap to produce copper intermediate products (black copper and blister copper) containing (75 to 88) and (90 to 99) percent copper, respectively.

Blast Furnace (Cupola)/Reverberatory Smelting Process (15). Low-grade scrap (irony copper and brasses, motor armatures, foundry sweepings, slags, drosses, and skimmings) is treated by the blast furnace (cupola)/reverberatory smelting process to recover the copper as an intermediate product--black copper--for further processing. In this process, two major pieces of equipment are used--the blast furnace and the reverberatory furnace. The blast furnace is used to purify the scrap, whereas the reverberatory furnace is used to separate the slag from the molten metal. The process steps for this process are: (a) charging of the blast furnace (cupola), (b) melting the charge, (c) mixing of molten mass, (d) tapping of slag and metal into the reverberatory furnace, (e) allowing slag and metal to separate into layers, and (f) tapping of slag and black copper melt. Afterwards, the molten melt of black copper is either cast into ingots or transferred in the molten state to the converter for further processing.

Energy required for this process is from coke which serves both as a reducing agent and a source of fuel.

Potential environmental pollutants produced by this process are atmospheric emissions, solid wastes, and liquid wastes. The atmospheric emissions are composed of gases and particulate matter. The gases are generated by the combustion of coke and burning of any organic constituents contained in the charge. Chemical composition will vary depending on the type of scrap but generally the gases will contain carbon dioxide, carbon monoxide, nitrogen, sulfur oxides, and possibly nitrogen oxides. The gases may also contain halogens and hydrocarbons, if present in the charge.

The particulate emissions are composed of a mixture of fumes, metal particles formed by the volatilization and condensation of metal values, and dusts removed from the furnace by entrainment in the gaseous emissions. These emissions normally contain such materials as zinc, lead, tin, copper, antimony, chlorine, and unburned carbon. Zinc is normally the major component.

Data are limited on the composition of particulate emissions from the blast furnace. However, baghouse dusts from one installation had the following composition:(7)

	Percent
Zinc	58-61
Lead	2-8
Tin	5-15
Copper	0.5
Antimony	0.1
Chlorine	0.1-0.5

At this installation, the cupola melt contained the following:

	Percent
Copper	75-88
Tin	1.5
Lead	1.5
Antimony	0.1-0.7
Iron	0.5-1.5
Zinc	4-10
Sulfur	0.5-1.25

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(7) Spendlove, M. J., Information Circular 8002, U. S. Dept. of Interior, Bureau of Mines (1961).

Emission factors vary depending on the composition of the charge. However, for treating scrap and residues, the emission factor is estimated at 50 lb per ton of charge.(8)

Solid wastes generated are slags and baghouse dusts (discussed above). Composition of the slag is variable depending on such factors as type of scrap and fluxing agent. However, the slag will normally have a composition approximating the following:

	Percent
Iron Oxide (FeO)	29
Calcium Oxide	19
Silica	39
Zinc	10
Copper	<1.5
Tin	0.7

It will represent approximately 5 percent of the charge.

Liquid wastes are generated as wastewater from cooling the blast furnace, in casting of the ingots, and quenching of the slag.

Thus, the blast furnace/reverberatory smelting process has a high potential for the production of serious pollution problems. These problems could result from pollution of the atmosphere and the water systems, if the wastes and emissions are not collected and disposed of in a nonpolluting manner.

Converter Smelting Process (16). Black copper is purified, i.e., the heavy metals concentration is lowered to produce an intermediate product containing 90 to 99 percent copper, by the converter smelting process. The process steps are: (a) charging of the converter with molten black copper, (b) blowing of the molten charge (blow 1), (c) deslagging, (d) blowing of molten charge (blow 2), and (e) removing the slag, if any is formed. Afterwards, the copper--blister copper--is poured and cast into ingots for refining or transferred in the molten state directly to the refining furnaces. Some produce the copper shot product by quenching the blister copper to form small pellets.

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(8) Vandegrift, A. E., et al., Particulate Pollutant System Study, Volume 1-Mass Emissions, Midwest Research Institute, Kansas City, Missouri (May 1, 1971).

Essentially no energy is required for this process. In fact, care must be taken to prevent overheating of the converter.

The process produces atmospheric emissions, solid wastes, and liquid wastes. The atmospheric emissions contain both particulate matter and gas. The particulate matter is composed of fumes (metal particles resulting from volatization and condensation of metal values) and dusts entrained in the gaseous emissions.

The major sources of particulate emissions are the charging-melting and blowing steps. Emission (furnace) factors for these steps are estimated at 30 and 39 lb of particulate matter per ton of charge processed, respectively. Emission factor for pouring is estimated at only 0.6 lb of particulates per ton of charge processed. Emission factor for casting is comparable to that for the pouring step. The high emission factors for the charging-melting and blowing steps result from the heavy evolution of fumes when the charge is loaded into the furnace and melted down and when the melt is fluxed with a gaseous fluxing agent (air).

Quantitative analytical data are not available on the composition of these emissions. However, qualitatively, the particulate emissions contain such metal values as tin, lead, antimony, iron, zinc, sulfur, copper, silicon, and calcium.

These emissions are in the form of dust and fumes. The dust is carried from the converter by entrainment in the "blowing" air, whereas the fumes result from volatization and condensation of the volatile metals. The fumes have a particle size in the sub-micron range. The dust particles are much larger, probably in the 5 to 20 micron range or larger. The particles have no definite shape, i.e., an irregular shape.

The atmospheric emissions can be controlled with baghouses, electrostatic precipitators, and scrubbers. Probably the most widely used device is the baghouse with control efficiency of approximately 95 percent.

Other wastes include solid waste and liquid wastes. The solid wastes generated are baghouse dusts and converter slags. Much of the solid wastes are recycled or treated for recovery of metal values. For example, the converter slags may be returned to reverberatory smelting (Process 15) for copper recovery. Liquid wastes are generated as wastewater from casting of the ingots, from wet scrubbers, if used, and from quenching of the slags.

Thus, this process can be a source of serious pollution problems, if the pollutants are not collected and disposed of in a nonpolluting manner.

Electric Smelting Process (17). This process is very similar to Processes 15 and 16 in that blister copper and black copper, intermediate products for refining by the electric smelting process operation, can be produced by both processes. The advantage of Process 17 over the combination of Processes 15 and 16 is that the quantity of atmospheric emissions, both gases and particulates, is significantly reduced. Using electricity in place of coke as the fuel and pure oxygen in place of air to oxidize the melt result in lower atmospheric emissions. Consequently, since much of the particulate emissions is carried from the smelting furnaces by entrainment in the gases, the reduced volume of gases results in a reduced amount of particulate matter. Thus, with the strong emphasis being placed on pollution abatement, this process is being viewed strongly as the preferred process for smelting of copper scrap.

The process steps for the electric smelting process, which are essentially the same as those for Processes 15 and 16, are: (a) charging of the electric furnace, (b) melting of the charge, (c) removing the slag, (d) adding high iron scrap and virgin copper, (e) blowing the melt (blow 1), (f) skimming to remove the slag formed by blow 1, (g) adding more flux, (h) blowing the melt (blow 2), (i) skimming to remove the slag formed by blow 2, and (j) transferring the melt to the holding furnace for fire-refining or casting as blister copper. In some cases, the copper is given a third blow termed the "finish blow".

The energy required for this process is the electricity necessary to melt the charge and drive the equipment. The heat evolved during the blowing is sufficient to keep the melt molten. In fact, in many cases, care must be taken to prevent overheating of the furnace.

Atmospheric emissions, liquid wastes, and solid wastes are generated by this process. The atmospheric emissions consisting of gases, fumes, and dusts are generated throughout the process. The process steps which are the major contributors are (1) charging of the furnace, (2) melting of the charge, and (3) blowing of the melt.

The composition of the emissions will vary depending on the composition of the charge. Normally, the gases contain sulfur oxides, nitrogen, carbon dioxide, and carbon monoxide. The particulate matter includes fumes and dusts composed of such metal values as zinc, lead, tin, copper, antimony, chlorine, unburned carbon, precious metals (gold and silver), and constituents making up the fluxes.

Particle size of the fumes and dusts ranges from 0.05 micron to approximately 1 micron for the fumes to approximately 5 microns or greater for the dusts. The dusts are readily collected using such devices as baghouses or electrostatic precipitators. Cyclones may be used in conjunction with these. However, because of the small particle size of the fumes, collection is difficult and much of the fumes pass on through the control devices into the atmosphere.

Emissions data are lacking and it is difficult to even estimate emission factors for this smelting process. However, it is estimated that the furnace emissions factors may range from about 80 to about 450 lb of particulates per ton of scrap processed. These estimates are based on the fact that the emission factor for smelting/refining in the brass and bronze segment was estimated at approximately 80 lb of particulates per ton of alloy produced,(9) and emissions factor for similar processing in the primary copper industry was estimated at approximately 450 lb of particulates per ton of copper produced.(10)

Solid wastes and liquid wastes generated by this process are the same wastes as generated by Processes 15 and 16. Data are lacking from which to calculate quantities. However, the slags contain such metal values as zinc, tin, lead, copper, iron, alumina, silica, antimony, and other nonvolatile metals present in the scrap and the fluxes. Many of the slags are recycled for copper recovery and the recovery of other metal values before being discarded. Liquid wastes from cooling of the equipment, quenching of the slags, and cooling of the ingots contain both soluble and suspended solids. These wastes are recycled, disposed of in settling ponds, or dumped into streams or sewers.

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(9) Spendlove, M. J., Methods for Producing Secondary Copper, U. S. Dept. of Interior, Bureau of Mines, Information Circular 8002, p 21 (1961).

(10) Vandegrift, A. E., et al., Particulate Pollutant System Study, Volume III, Handbook of Emission Properties (pp 203,522), p 262 May 1, 1971).

Thus, this process produces waste products which can cause serious pollution problems if the wastes are not collected and disposed of in a nonpolluting manner.

Refining/Casting Operation

Blister copper, black copper, and high grade copper scrap are purified by the refining/casting operation. The products from this operation containing approximately 99.9 percent copper are: (1) fire-refined copper cast as ingots, billets, slabs, cakes, and bars for manufacturing plates, sheets, rods, and copper base alloys; (2) electrolytically refined copper cast as billets, wire bars, ingots, or cakes; (3) O.F.H.C. copper (oxygen-free high conductivity copper); and (4) copper powder. These are produced by Processes 18 through 25 as shown in the copper segment flowsheet.

Fire-Refining Process (18). The final purification of scrap copper may be achieved by the fire-refining process. The process steps are: (a) charging the furnace which may be either a reverberatory or cylindrical tilting type; (b) melting the charge in an oxidizing atmosphere until the melt begins to "work", i.e., begins to bubble and liberate sulfur oxides; (c) skimming the melt; (d) blowing the melt with air; (e) covering the melt with a reducing agent such as coke, charcoal, or coal (anthracite); (f) poling with green wooden poles; (g) skimming, if necessary; (h) pouring; and (i) casting into ingots, slabs, wire bars, and billets. In some cases, molten metal from the smelting operation is charged directly to the reverberatory furnace. In regard to (f) above, the green poles used are largely maple and birch. They are approximately 10 inches in diameter at the base, at least 20 feet long, and weigh approximately 200 lb. Maple is preferred because it burns more slowly than other woods. The quantity of green poles consumed varies depending on the degree of reduction necessary. In the manufacture of wire bars from scrap copper, approximately 100 lb of poles per ton of copper are required.(11) As an alternative natural gas is being developed and in some cases may be used in place of green poles.

Energy required for this process is that necessary to keep the melt molten.

Atmospheric emissions, solid wastes, and liquid wastes are produced by this process. Essentially each process step is a source of atmospheric emissions which are composed of gases and particulate matter made up of fumes and dusts.

Emissions data are lacking for the fire-refining process. However, based on the chemistry involved and the composition of the melt, the gases are known to contain sulfur oxides, carbon dioxide, nitrogen, carbon monoxide, and most likely, hydrocarbons if green poles are used, or methane if natural gas is used in the reduction phase of the refining. The particulate emissions volatilized as fume or carried from the furnace by entrainment in the gases contain such metal values as zinc, tin, copper, lead, and others contained in the melt. In addition, the emissions may also contain unburned carbon and materials from the fluxing agents.

The atmospheric emissions are controlled with baghouses, electrostatic precipitators, or wet scrubbers. A cyclone may be used in conjunction with these devices.

Other wastes generated by the process are solid wastes and liquid wastes. The solid wastes are slags containing the fluxing materials and metal impurities from the black, blister, and scrap copper and the impurities from the green poles. The liquid wastes are cooling wastewater from cooling or quenching of the castings and cooling of the furnace. The water contains soluble phosphate used to condition the molds and the inhibitor from the cooling water.

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(11) Schench, W. A., et al., Trans. AIME, Institute of Metals Division, p 299 (1930).

Although emission factor data are not available, this process does generate large quantities of materials which can cause serious atmospheric and water pollution problems.

Fire (Partial) Refining Process (19). When the copper is to be cast into anodes, an intermediate product for electrolytic refining, the melt is not completely fire-refined by oxidizing and poling. Instead, the copper is partially fire-refined and cast into anodes. The anodes contain about 99 percent copper and small amounts of silver, gold, lead, selenium, tellurium, and other metals.

The process steps, energy required, pollutants generated, emission factors, and control of pollutants are essentially the same for this process as for the full fire-refining process, Process 18.

This process does generate significant quantities of potential environmental pollutants and is, therefore, a source of potential pollution problems.

Electrolytic Refining Process (20). Partial fire refined copper--anodes--is converted to high purity copper cathodes by the electrolytic refining process. The impurities in the anode copper either dissolve in the electrolyte or fall to the bottom of the cells as slime. The slimes may contain such impurities as sulfur, arsenic, antimony, lead, nickel, selenium, tellurium, gold, and silver, if present in the anode copper. The cathode copper assaying about 99.9+ percent copper contains trace quantities of the above impurities and is the intermediate product for Processes 21, 22, and 23 for the production of electrolytic refined copper product and for the production of copper powder.

The process steps for the electrolytic refining process are: (a) making up the electrolyte containing water, sulfuric acid, copper sulfate, and addition agent; (b) placing the copper anode in the electrolyte bath as one of the electrodes--the anode; (c) dissolving the anode; (d) depositing the copper on the starting sheets--the cathode; (e) removing the cathode for melting and casting; (f) regenerating the spent electrolyte; and (g) removing slimes for recovery of metal values.

Energy required for this process is electricity to produce the cathodes and to drive the equipment.

This process produces essentially no atmospheric emissions if the anode copper does not contain arsenic. If arsenic is present, arsine (AsH_3) is formed and evolved during electrolytic refining of copper. This has not presented a serious problem for the operators as the tank houses are generally well ventilated and the arsine is ejected outside the house. However, arsine formation can be a problem in electrolyte regeneration.

The major wastes produced are solid wastes (aqueous slurries composed of the slime) and liquid wastes (spent electrolyte). The slimes are sent to precious metal recovery where such metal values as gold, silver, nickel, and lead are recovered. A "black liquor", liquid waste, is formed during electrolyte purification. This material is either discarded, generally after neutralization, or used in leaching operations in associated plants. Additional liquid wastes are generated during recovery of nickel, iron, zinc, and other metal values from the spent electrolyte.

Thus, the electrolytic refining process can present serious pollution problems. Arsine, an atmospheric pollutant which is volatile and poisonous, is generated, if arsenic is present in the cathodes. Furthermore, large quantities of liquid wastes and solid wastes are generated which can cause water pollution problems.

Electric Melting Process (21). Cathode copper is melted and cast into the desired shape by the electric melting process. Normally, the process steps are: (a) feeding the cathodes into the furnace through a charge slot to maintain a molten bath; (b) removing molten copper from the tap hole; and (c) casting the molten copper as billets, wire bars, ingots, or cakes. Periodically, flux is added to the melt to refine the copper and slag is removed as the waste product.

Energy required is the electricity to melt the copper and drive the auxiliary equipment.

Wastes generated by this process are small amounts of atmospheric emissions, liquid wastes, and solid wastes. The atmospheric emissions result primarily from the evolution of gases from the melting operation and from pouring and casting of the pure copper. The solid wastes are the slags or skimmings from the melting furnace, whereas liquid wastes are formed during ingot casting and cooling of the equipment.

Emissions data are not available for this process. It is expected that this process would constitute a minor source of pollution problems in this segment of the secondary nonferrous metals industry.

Reverberatory Melting Process (22). This process is an alternative process for converting cathode copper intermediate product to the desired shapes of electrolytic refined copper. The process steps are: (a) charging the reverberatory furnace, (b) melting the cathodes, (c) blowing (flapping) of melt, (d) skimming of melt, (e) poling of melt, (f) skimming of melt, (g) pouring, and (h) casting.

Energy required is the fuel to melt and keep the charge molten and that required to drive the auxiliary equipment.

Atmospheric emissions, liquid wastes, and solid wastes are produced by this process. The atmospheric emissions--gases, fumes, and dusts--are formed during each processing step with the majority of the emissions being evolved during blowing (flapping) and poling of the melt. Emissions data are not available on the quantity and composition of these emissions; however, it is expected that the emissions contain gases such as carbon dioxide, carbon monoxide, sulfur oxides, and hydrocarbons. The fumes and dusts are composed of, primarily, copper, and small quantities of such metal values as lead, nickel, selenium, and tellurium.

Liquid wastes result from casting of the melt into the desired shapes and from cooling of the equipment. These liquid wastes, primarily wastewater, contain soluble inhibitors and insoluble solids such as the bone ash to condition the molds. In some cases, phosphates may be used.

Solid wastes are the slags or skimmings formed and removed from the melt during the melting (refining) of the cathodes. These wastes contain the impurities from the cathode copper and the fluxes, if added.

In view of the waste products and emissions generated by this process, pollution problems can result if these pollutants are not collected and disposed of in a nonpolluting manner. However, it is expected that this process is a minor source of pollution problems when compared to some of the other processes.

Induction Melting Process (23). Oxygen-free-high-conductivity (O.F.H.C.) copper is produced by the induction melting process using cathodes as the source of copper. The O.F.H.C. copper is oxygen-free with a reported purity of 99.99 percent. The process steps are: (a) clean the cathodes, (b) preheat the cathodes in an atmosphere of reducing gas which is low in hydrogen, (c) melt the clean, preheated cathodes in a low-frequency induction heater, (d) cover the melt with graphite granules, (e) discharge molten copper to a low-frequency induction-heated "pour hearth" which distributes the copper to the casting machine, and (f) cast the O.F.H.C.* copper. A nonoxidizing atmosphere is maintained throughout melting and casting.

Energy required is the electricity to melt the cathodes and keep the melt molten and to operate the auxiliary equipment.

Waste products produced by this process are atmospheric emissions, solid wastes, and liquid wastes. The atmospheric emissions are produced during preheating of the cleaned cathodes, melting of the cathodes, and casting of the copper melt into ingots and other shapes. Emissions data are not available; however, the emissions no doubt consist of reducing gases and carbon monoxide from melting of the cathodes. The gases contain a small quantity of particulate matter which is composed of copper along with other metals found in the melt and graphite particles. The solid waste is basically graphite used to cover the melt. The liquid wastes are wastewater used in the casting of the melt and cooling of the equipment.

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* O.F.H.C. is a trade name of the U. S. Metals Refining Company and also means oxygen free high purity copper.

This process produces minor quantities of potential environmental pollutants. Therefore, the process has little or no potential for producing serious pollution problems.

Electrolytic Winning Process (24). Copper in the form of impure copper cathode, an intermediate product to electrolytic refining process, is recovered from copper sulfate solutions by the electrolytic winning process. The deposit is not as pure as the cathodes from the electrolytic refining process and, therefore, must be purified. The process steps are: (a) prepare electrolyte, (b) electrolytically deposit the copper on thin copper starter sheets, (c) remove the copper cathodes from the electrolytic cells, (d) clean cathodes by soaking in water, (e) replace copper starter strips, (f) regenerate electrolyte, and (g) repeat series of above steps. Spent electrolyte is is continuously bled from the system, regenerated, and returned.

Energy required is the electricity to operate the process.

The waste products generated by the process are primarily liquid waste consisting of spent electrolyte and solid wastes consisting of slimes formed during the electrolysis and resulting from regeneration of the electrolyte. If the electrolyte contains arsenic, gaseous arsine (AsH_3) is liberated. This material is generally vented to outside of the building.

Emissions data are lacking. However, from data which are available on electrolytic refining, most likely, the waste products produced by the electrolytic refining process can cause water pollution problems.

Electrolytic Powder Production Process (25). Copper powder is prepared from copper sulfate solutions by the electrolytic powder production process using pure copper cathodes from the electrolytic refining process as the source of copper. The process steps are: (a) prepare electrolytic cell for powder production using cathode copper as the anode, (b) electrolytically deposit copper powder,

(c) remove copper powder from cell, (d) return electrolyte to cell, (e) wash electrolyte from copper powder, (f) heat powder in hydrogen-carbon monoxide atmosphere to remove water, (g) classify dried powder, (h) blend powders of different particle size to obtain correct particle size distribution, and (i) package product.

Energy required is the electricity to produce the copper powder and drive the equipment and the fuel to heat the dryer.

Waste products produced by this process are atmospheric emissions and liquid wastes. The atmospheric emissions contain gases composed of water vapor, carbon monoxide, hydrogen, possibly arsine, and unburned fuel. The particulate portion of the atmospheric emissions is copper powder from the dryer, blender, and classifier.

The liquid waste is the spent electrolyte from the electrolytic cell and wash liquor from washing the copper powder. The spent liquor is normally regenerated and recycled to the electrolytic cell. The wash liquor containing sulfuric acid, water, and some soluble copper is probably neutralized and disposed of in a holding pond.

Thus, waste products produced by this process can cause pollution problems if not properly controlled.

Population of Secondary Copper Processors

(1) Barth Smelting Corporation
99-129 Chapel Street
Newark, New Jersey
Telephone: (201) MA2-4908

(2) Batchelder-Blasius, Inc.
Post Office Box 5503
Spartanburg, South Carolina
29301
Telephone: (803) 439-6321

(3) Bay State Refining, Inc.
Chicopee Falls, Massachusetts

(4) Joseph Behr and Sons, Inc.
1100 Seminary Street
Rockford, Illinois
Telephone: (815) 962-7721

(5) Belmont Smelting and Refining
Works, Inc.
320 Belmont Avenue
Brooklyn, New York
Telephone: DI2-4900

(6) W. J. Bullock, Inc.
Post Office Box 539
Fairfield, Alabama

(7) Cerro Corporate Brass Company
Division of Cerro Corporation
16600 St. Clair Avenue
Cleveland, Ohio 44110
Telephone: (216) 481-3000

(8) Circuit Foil Corporation
23 Amboy Road
Bordentown, New Jersey
Telephone: (609) 298-4800

(9) Colonial Metals Company
Columbia, Pennsylvania
Telephone: (717) 684-2311

(10) General Copper and Brass Company
Post Office Box 5353-D
Philadelphia, Pennsylvania
Telephone: SA6-7111

(11) Samuel Greenfield Company,
Inc.
Stone and Ingot Streets
Brooklyn, New York

(12) Holstead Metal Parts, Inc.
West Newcastle Street
Zelienople, Pennsylvania
16063
Telephone: (412) 452-6500

(13) Benjamin Harris & Company
Eleventh and State Streets
Chicago Heights, Illinois
Telephone: SK5-0573

(14) Henning Brothers & Smith,
Inc.
91-115 Scott Avenue
Brooklyn, New York

(15) K. Hettleman & Sons,
Division of Minerals and
Chemicals
Phillip Corporation
Ninth Street and Patapsco
Avenue
Baltimore, Maryland 21225
Telephone: (301) 355-0770

(16) Holtzman Metal Company
5223 McKissock Avenue
St. Louis, Missouri 63147

(17) H. Kramer & Company
1339-59 West 21st Street
Chicago, Illinois 60608
Telephone: CA6-6600

(18) Metal Bank of America, Inc.
6801 State Road
Philadelphia, Pennsylvania
19135
Telephone: (215) 332-6600

(19) Nassau Smelting and Refining Co., Inc.
5 Nassau Place
Tottenville, New York
Telephone: (212) YU4-1970

(20) Phelps Dodge Refining Corporation
300 Park Avenue
New York, New York
Telephone: 751-3200

(21) Riverside Alloy Metal Division
H. K. Porter Company, Inc.
309 Porter Building
Pittsburgh, Pennsylvania 15219
Telephone: (412) 391-1800

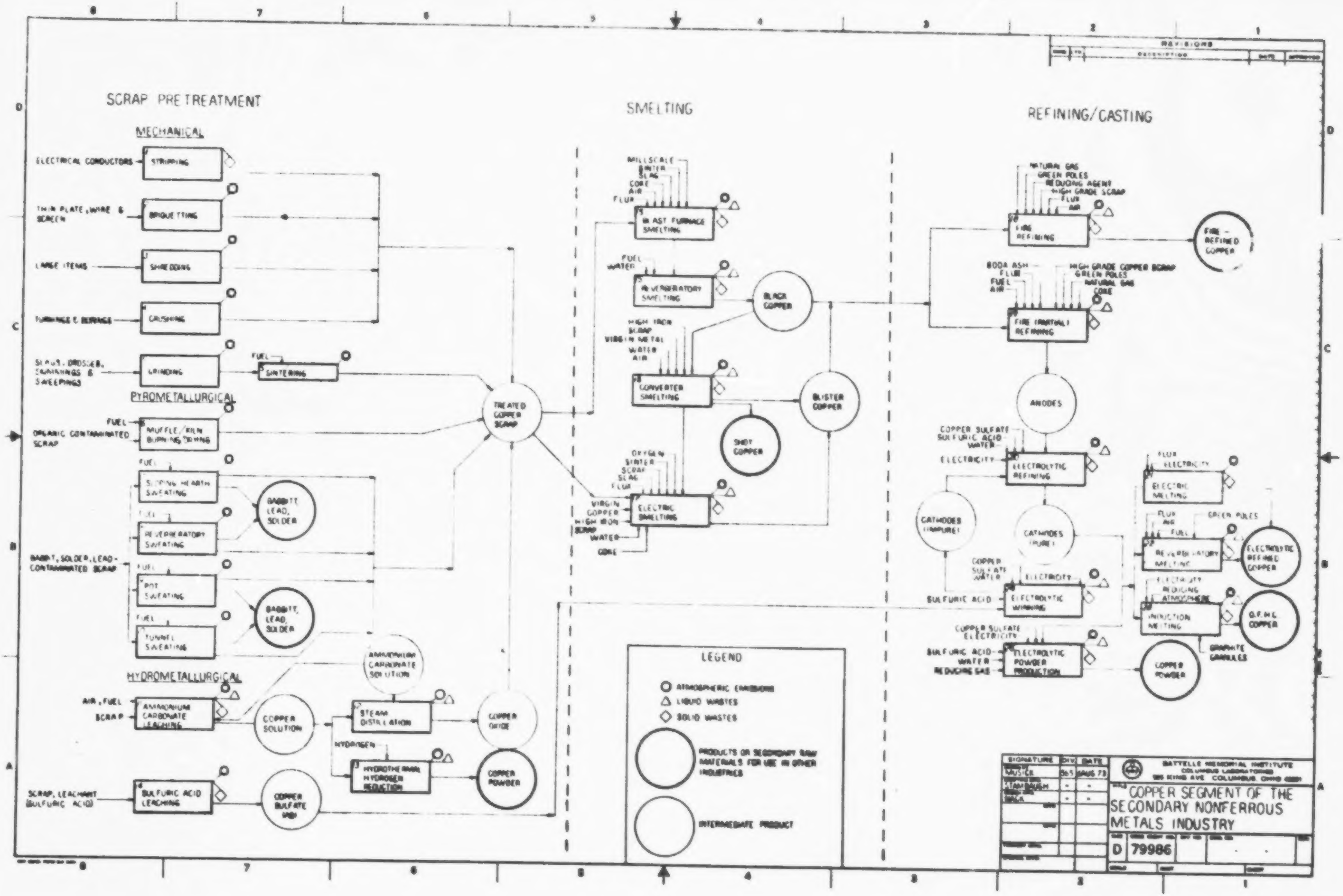
(22) Roessing Bronze Company
320 Barbour
Pittsburgh, Pennsylvania

(23) I. Schumann & Company
4391 Bradley Road
Post Office Box 2219
Cleveland, Ohio

(24) M. Seligman & Company
3401 S. Lawndale Avenue
Chicago, Illinois

(25) SIPI Metals Corporation
1722 N. Elston Avenue
Chicago, Illinois

(26) U. S. Metals Refining Company
1217 Avenue of Americas
New York, New York 10020
Telephone: (212) PL7-9700


SCRAP PRETREATMENT
MECHANICAL
ELECTRICAL CONDUCTORS
STRIPPING
THIN PLATE, WIRE & SCREEN
BRIQUETTING
LARGE ITEMS
SHREDDING
TURNINGS & BORINGS
CRUSHING
SLAGS, DROSSES, SKIMMINGS & SWEEPINGS
GRINDING
FUEL
SINTERING
PYROMETALLURGICAL
FUEL
ORGANIC CONTAMINATED SCRAP
MUFFLE/KILN BURNING/DRYING
FUEL
SLOPING HEARTH SWEATING
FUEL
REVERBERATORY SWEATING
BABBITT, LEAD, SOLDER
BABBITT, SOLDER, LEAD-CONTAMINATED SCRAP
FUEL
POT SWEATING
FUEL
TUNNEL SWEATING
BABBITT, LEAD, SOLDER
HYDROMETALLURGICAL
AIR, FUEL
SCRAP
AMMONIUM CARBONATE LEACHING
AMMONIUM CARBONATE SOLUTION
COPPER SOLUTION
STEAM DISTILLATION
COPPER OXIDE
HYDROGEN
HYDROTHERMAL HYDROGEN REDUCTION
COPPER POWDER
SCRAP, LEACHANT (SULFURIC ACID)
SULFURIC ACID LEACHING
COPPER SULFATE (AQ)
TREATED COPPER SCRAP
SMELTING
MILLSCALE
SINTER
SLAG
CORE
AIR
FLUX
BLAST FURNACE SMELTING
FUEL
WATER
REVERBERATORY SMELTING
BLACK COPPER
HIGH IRON SCRAP
VIRGIN METAL
WATER
AIR
CONVERTER SMELTING
BLISTER COPPER
SHOT COPPER
OXYGEN
SINTER
SCRAP
SLAG
FLUX
VIRGIN COPPER
HIGH IRON SCRAP
WATER
COKE
ELECTRIC SMELTING
REFINING/CASTING
NATURAL GAS
GREEN POLES
REDUCING AGENT
HIGH GRADE SCRAP
FLUX
AIR
FIRE REFINING
FIRE-REFINED COPPER
SODA ASH
FLUX
FUEL
AIR
HIGH GRADE COPPER SCRAP
GREEN POLES
NATURAL GAS
COKE
FIRE (PARTIAL) REFINING
ANODES
COPPER SULFATE
SULFURIC ACID
WATER
ELECTRICITY
ELECTROLYTIC REFINING
CATHODES (IMPURE)
CATHODES (PURE)
COPPER SULFATE
WATER
ELECTRICITY
SULFURIC ACID
ELECTROLYTIC WINNING
COPPER SULFATE
ELECTRICITY
SULFURIC ACID
WATER
REDUCING GAS
ELECTROLYTIC POWDER PRODUCTION
COPPER POWDER
FLUX
ELECTRICITY
ELECTRIC MELTING
FLUX
AIR
FUEL
GREEN POLES
REVERBERATORY MELTING
ELECTROLYTIC REFINED COPPER
ELECTRICITY
REDUCING ATMOSPHERE
INDUCTION MELTING
O.F.H.C. COPPER
GRAPHITE GRANULES
LEGEND
○ ATMOSPHERIC EMISSIONS
△ LIQUID WASTES
◇ SOLID WASTES
PRODUCTS OR SECONDARY RAW MATERIALS FOR USE IN OTHER INDUSTRIES
INTERMEDIATE PRODUCT
REVISIONS
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STAMBAUGH
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79986

BATTELLE MEMORIAL INSTITUTE
COLUMBUS LABORATORIES
505 KING AVE COLUMBUS, OHIO 43201

COPPER SEGMENT OF THE SECONDARY NONFERROUS METALS INDUSTRY

PROCESS DESCRIPTION OF THE GERMANIUM SEGMENT OF THE SECONDARY NONFERROUS METALS INDUSTRY

Annual production volume of secondary germanium is about 8000 pounds. Because of the high cost of germanium (~$50/lb), process losses through air, solid waste, and water emissions are reduced to a minimum. Also, the emphasis placed on the highest possible purity of the final product insures that all processing operations are conducted in closed systems to prevent atmospheric contamination of the product.

Raw Materials

Germanium scrap sources are as follows:

(1) Solid scrap (100 percent solid metal) obtained as scrap ends from zone refining
(2) Slicing compounds from single crystals obtained as sludge containing 50 to 80 percent germanium
(3) Acid etching scrap
(4) Grindings and polishing wastes from the infrared industry
(5) Scrap from the electronic industry.

Products

High purity germanium is the only product of this segment.

Process Description

One manufacturing operation--hydrometallurgical refining--is involved in the processing of germanium scrap. This operation and the processes involved in it are shown in the process flowsheet of this segment.

Hydrometallurgical Refining Manufacturing Operation

This operation involves three processes--chlorination, hydrolysis, and hydrogen reduction. These are discussed in detail below.

Chlorination Process (1). In this process, germanium is converted to germanium tetrachloride. The process steps are (1) charge scrap to vessel, (2) heat and add sodium chloride.

The volatilized tetrachloride with any impurities is distilled to get germanium tetrachloride.

The process requires minor amounts of heat energy.

Small quantities of gaseous wastes are generated.

The emissions are water scrubbed and the solids recycled. Scrubber water is also recycled.

The process has no significant pollution potential.

Hydrolysis Process (2). This process converts the tetrachloride to germanium dioxide by ice water hydrolysis.

Details of the process steps are not known.

Minor amounts of water waste (with insignificant pollution potential) are generated.

Hydrogen Reduction Process (3). This process converts the germanium dioxide to the pure metal.

The process steps are (1) pass hydrogen, (2) heat to 650 C.

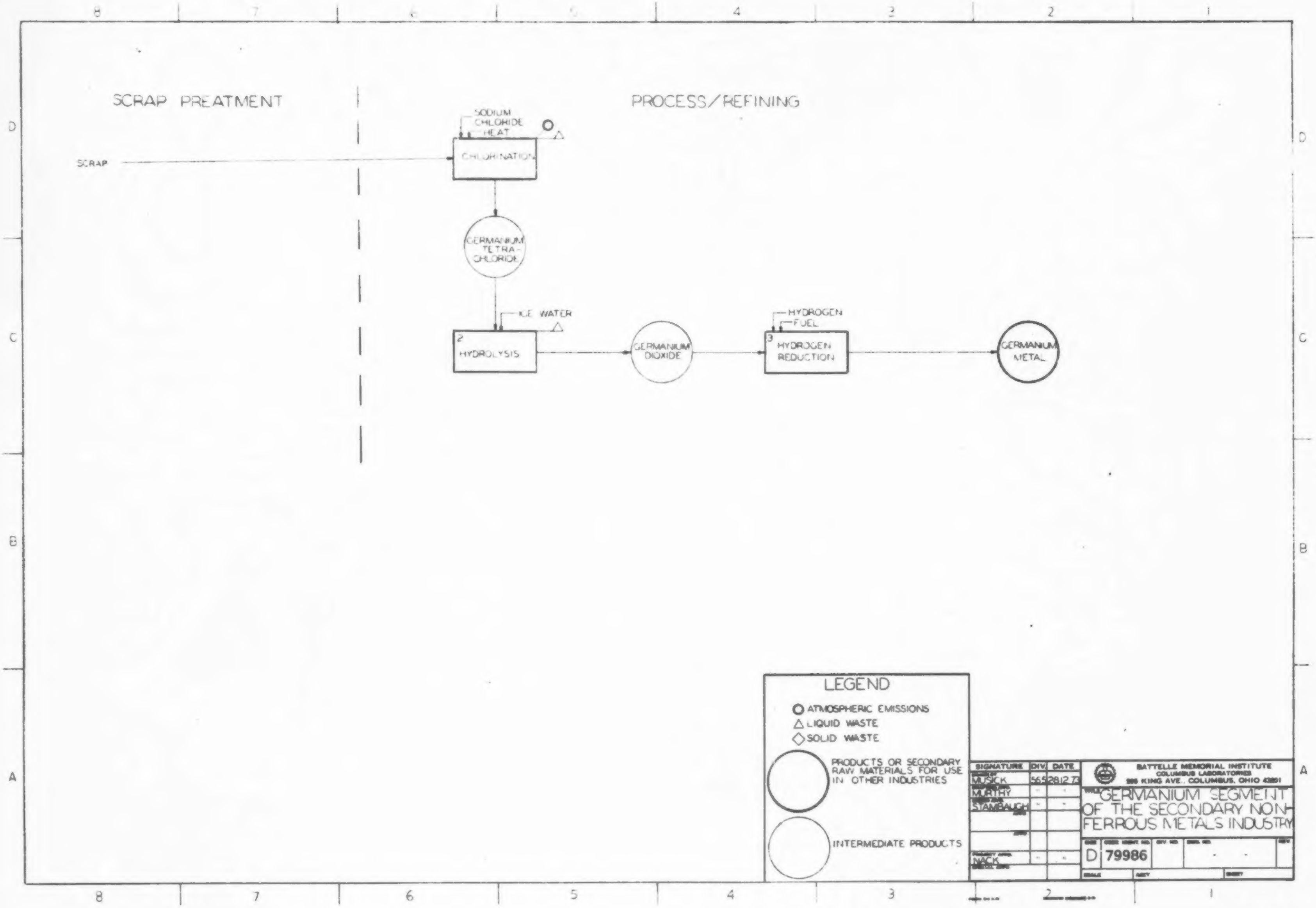
Heat energy is utilized in this process.

The process produces no pollutants.

Population of Secondary Germanium Processors

(1) Belmont Smelting and Refining Works
320 Belmont Avenue
Brooklyn, New York

(2) Kawecki Berylco Industries
(KBI)
220 East 42nd Street
New York, New York 10017
(212) 682-7143.


SCRAP PREATMENT
PROCESS/REFINING
SCRAP
SODIUM CHLORIDE
HEAT
CHLORINATION
GERMANIUM TETRA-CHLORIDE
ICE WATER
2 HYDROLYSIS
GERMANIUM DIOXIDE
HYDROGEN
FUEL
3 HYDROGEN REDUCTION
GERMANIUM METAL
LEGEND
○ ATMOSPHERIC EMISSIONS
△ LIQUID WASTE
◇ SOLID WASTE
PRODUCTS OR SECONDARY RAW MATERIALS FOR USE IN OTHER INDUSTRIES
INTERMEDIATE PRODUCTS
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281273
MURTHY
STAMBAUGH
NACK
BATTELLE MEMORIAL INSTITUTE
COLUMBUS LABORATORIES
505 KING AVE. COLUMBUS, OHIO 43201
GERMANIUM SEGMENT OF THE SECONDARY NON-FERROUS METALS INDUSTRY
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PROCESS DESCRIPTION OF THE HAFNIUM SEGMENT OF THE SECONDARY NONFERROUS METALS INDUSTRY

Since hafnium occurs in nature with zirconium, both hafnium and zirconium are processed and isolated in the same facility. The quantity of hafnium marketed in the U. S. is very small (less than a million ounces).

Hafnium is not a toxic metal. Due to the high unit price of the metal, recovery is maximized by excellent waste control.

These considerations indicate the environmental pollution problems from the secondary hafnium industry are insignificant.

Details of the process are difficult to obtain because of the desire of the U. S. hafnium processors to protect the proprietary nature of their process.

Population of Secondary Hafnium Processors

(1) Amax Speciality Metals Division
American Metal Climan, Inc.
6000 Hake Road
Akron, New York 14001
Telephone: (716) 542-5454

(2) Teledyne Wah Chang
P. O. Box 460-T
Albany, Oregon

PROCESS DESCRIPTION OF THE INDIUM SEGMENT OF THE SECONDARY NONFERROUS METALS INDUSTRY

Efforts to obtain information on this segment have not been as successful as in other areas. The Indium Corporation of America is the only producer of secondary indium and information obtained from this company is summarized below.

(1) The total annual U. S. production (1972) of both primary and secondary indium is less than 2 million ounces (<62 tons). The market value of indium is about $4.50 per ounce. This high cost of indium makes the recovery process very profitable and necessary.

(2) The process of recovery of indium consists of using a small blast furnace followed by a series of typical chemical and electrical recovery processes, details of which are proprietary.

(3) Indium is not toxic. There are no environmental problems or emissions.

(4) The industry is not interested in any external assistance in research and development work. The entire process is proprietary. The industry is very careful to protect that status.

Population of Secondary Indium Processors

The Indium Corporation of America
1676-1680 Lincoln Avenue
Utica, New York 13502
Telephone: (315) 797-1630

PROCESS DESCRIPTION OF THE LEAD SEGMENT OF THE SECONDARY NONFERROUS METALS INDUSTRY

Introduction

This segment of the secondary nonferrous metals industry ranks second in consumption of scrap materials. In 1971,(1) 784,700 tons of lead scrap were consumed. In the recovery of the lead value from scrap, waste products are generated in the form of atmospheric emissions, liquid wastes, and solid wastes. These materials can cause pollution problems.

Raw Materials

The principal sources of lead scrap are:(2)

Soft lead
Hard lead
Cable lead
Battery-lead plates
Mixed common babbits
Solder and tinny lead
Type metals
Drosses and residues.

New scrap in the form of purchased drosses and residues make up 18 percent (143,400 tons) of the total. The remainder, old scrap, is predominantly battery scrap with small amounts of the other scrap. The scrap is essentially all from domestic sources. In addition to containing metallic lead or compounds and alloys of lead, the scrap contains a variety of organic materials such insulation, grease, and oil. Common alloying agents found in the scrap are tin, antimony, arsenic, cadmium, copper, indium, silver, zinc, tellurium, and bismuth.

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(1) Ryan, J. P., Minerals Yearbook, U. S. Dept. of Interior, Bureau of Mines, Vol. I, p 671 (1973).

(2) ibid, p 683 (1973).

Products

Products from the lead segment of the secondary nonferrous metals industry are: (1) lead ingots (pure/soft), (2) lead ingots (hard/semisoft), (3) lead ingots (alloys), (4) lead oxide (battery lead oxide), and (5) lead pigments (Pb_3O_4 and PbO).

Process Description

Lead is recovered from lead scrap by three manufacturing operations: (1) scrap pretreatment, (2) smelting, and (3) refining/casting. These operations and the processes associated with each operation are shown in the flowsheet entitled "Lead Segment of the Secondary Nonferrous Metals Industry".

Scrap Pretreatment Operation

In this operation, the lead scrap is treated to make it more amenable to further processing. This treatment involves densification and/or partial removal of metallic and nonmetallic contaminants.

Battery Breaker Process (1). The major source of lead is obsolete automobile batteries. By this process, the lead is separated from the nonmetallic portion of the battery. The process steps are: (a) draining the battery if not received dry, (b) breaking (crushing) the battery to break the lead portion from the nonlead portion, and (c) separating the lead from the battery case. This lead scrap in this form can be fed into the reverberatory or blast furnace for further processing and recovery of the lead.

Energy required for this process is that to drive the equipment.

agents found in the scrap are tin, antimony, arsenic, cadmium, copper, indium, silver, zinc, tellurium, and bismuth.

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Energy required for this process is that to drive the equipment.

Waste products generated are primarily liquid wastes and solid wastes. A small quantity of dusts may be generated if the batteries are treated dry. These dusts are composed of dirt, plastic, or battery case materials and lead compounds such as lead oxide and lead sulfate.

The liquid wastes are composed of sulfur acid, water, lead compounds, and the alloying agents from the lead plates.

The solid wastes, which make up the bulk of the waste products from this process are composed of the organic materials used in battery case fabrication. In addition, these solid wastes contain some sulfuric acid and lead compounds.

In view of the waste products generated by this process, serious pollution problems can arise if the wastes are not disposed of in a nonpolluting manner.

Crushing Process (2). Much of the drosses, residues, and possibly slags are received in large pieces, i.e., larger than desired for further processing. These scrap materials are crushed with jaw crushers to a suitable size. The process steps are: (a) load the crusher and (b) crush the scrap. Afterwards, the scrap is removed and further processed to recover the lead content.

Energy required is limited to that necessary to drive the equipment.

Waste products from this process are dusts resulting from the handling and crushing of the scrap.

Emissions data are not available. However, significant quantity of emissions could be generated. Therefore, the process can present pollution problems, if the dusts are not collected.

Rotary/Tube Sweating Process (3). Lead sheathed cable and wire, aircraft tooling dies, type metal drosses, and lead dross and skimmings are treated by the rotary/tube sweating process to recover the lead value. The process steps are: (a) charge the furnace with the scrap, (b) melt the lead value, (c) collect the molten lead,

(d) cast the molten lead, and (e) remove the residue from the furnace.

Energy required for this process is the fuel to heat the rotary furnace or sweating tube and electricity to drive the equipment.

Atmospheric emissions and solid wastes are generated by this process. The emissions contain gases composed of sulfur oxides, entrained air, nitrogen oxides, and the fuel combustion products. The particulate portion of the atmospheric emissions is composed of fumes, dusts, unburned fuel, soot, and fly ash. Furnace atmospheric emissions data are not available. However, based on data from similar processes, emissions factors are estimated to range from 70 lb of particulates per ton of metal processed (raw emissions factor for rotary reverberatory furnace smelting of lead)(3) to 32 lb of particulates per ton of scrap processed(4) (raw emissions factor for sweating of residual zinc).

Particle size of the emissions varies. The larger particles (dusts) are probably in the 5 to 20 micron or larger range, whereas the unagglomerated lead fumes vary in diameter from 0.07 to 0.4 micron with a mean particle size of 0.3 micron.(5)

Solid wastes are the metallic and nonmetallic portion of the scrap after removal of the lead.

As significant quantities of atmospheric emissions and solid wastes are generated by this process and since lead and lead compounds are toxic or hazardous materials, the waste products from this process can cause serious pollution problems if the waste products are not controlled. Failure to control the atmospheric emissions can result in pollution of the atmosphere, whereas disposal of the solid wastes in an unapproved manner can result in water pollution.

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(3) Vandegrift, et al., Particulate Pollutant System Study, Vol. III, Handbook of Emission Properties, Midwest Research Institute, Kansas City, Missouri, p 406 (May 1, 1971).

(4) Herring, W. O., Secondary Zinc Industry, Emission Control Problem Definition Study, APCO, EPA, Durham, North Carolina, p V1-22.

(5) Air Pollution Engineering Manual, U. S. Dept. HEW, NCAPA, Cincinnati, Ohio, p 307 (1967).

Reverberatory Sweating Process (4). This process is normally used to sweat scrap containing high lead content such as lead battery plates. The process steps are the same as for Process 3.

Energy required is the fuel--gas or oil--to heat the furnace.

Waste products from this process are atmospheric emissions and solid wastes. The atmospheric emissions are composed of gases and particulate matter containing both fumes and dusts. The gases discharged from the furnace contain the combustion products, sulfur oxides, unburned fuel, and hydrocarbons from pyrolysis of the organic compounds present in the scrap. The fumes and dusts contain metallic materials such as lead, antimony, and other heavy metals used to prepare the lead alloys, and nonmetallic materials such the fluxes and carbon or other organic contaminants from the scrap.

Although emissions data are lacking, it is estimated based on data from similar processes that raw emissions factor for the reverberatory sweating process will range from approximately 30 lb per ton of charge to 70 lb per ton of metal processed.(3,4)

Unagglomerated lead oxide fume particles vary in diameter from 0.07 to 0.04 micron with a mean diameter of about 0.3 micron. The particle size of the dust is expected to be much larger, normally in the 5 to 20 micron or larger size range.(5)

The atmospheric emissions are controlled by the same system as is used for the smelting operation and discussed under Process 5.

Solid waste materials are the residues remaining after removal of the lead. Composition of these wastes may vary somewhat, but generally will contain lead and other heavy metals such as antimony.

This process has a high potential for the production of pollution problems if emissions are not controlled.

Smelting Operation

Pretreated scrap is partially refined, i.e., some of the metallic and nonmetallic contaminants are removed by the smelting operation. The individual processes (5 and 6) comprising the smelting operation are shown in the attached flowsheet.

Reverberatory Smelting Process (5). Lead scrap (pretreated or untreated, mixed) is partially purified and densified by the reverberatory smelting process. This is achieved by the following process steps: (a) charge the furnace with the lead scrap and flue dusts, (b) melt the scrap, (c) allow the antimonical slag to rise to the surface of the melt, (d) tap the antimonical slag to the blast furnace, and (e) tap the molten lead melt to the refining/casting operation. Alternately, the molten lead may be poured and cast into ingots as a semisoft/hard lead product.

The energy required for this step is from the fuel oil or gas to smelt the scrap.

Atmospheric emissions are produced by this process. No solid or liquid wastes are produced.

The atmospheric emissions are composed of gases and particulate matter. The gases contain the products from combustion of the fuel and sulfur oxides along with any other gases from the scrap. The particulate matter (fume) is composed of oxides, sulfides, and sulfates of lead, tin, arsenic, copper, and antimony. Recoverable lead from the charge is about 47 percent. Approximately 46 percent of the charge is slag and 7 percent is fumes and dusts.

The unagglomerated particulate matter was found to have a particle size range of 0.07 to 0.4 micron with a mean value of 0.3 micron. The particle shape was essentially spherical.(6)

The reverberatory smelting process accounts for approximately 75 percent of the emissions from the lead segment of the secondary nonferrous metals industry. Particulate emission factor for reverberatory smelting is estimated at 130 lb (uncontrolled) and 1.6 lb (controlled) per ton of metal processed. Raw sulfur oxide emission factor is estimated at 85.0(7,8,9) lb to 190(10) lb per ton of metal processed.

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(6) Air Pollution Engineering Manual, U. S. Dept. HEW, NCAPC, Cincinnati, Ohio, pp 301-302 (1967).

Particulate emissions from this process are controlled with a baghouse, scrubber, or both. The baghouse is arranged as the final collector. These systems also include auxiliary items such as gas cooling devices and settling chambers. Sulfur oxide emissions are controlled in some plants with a wet scrubber.

The process produces significant quantities of atmospheric emissions and is, therefore, a potential source of pollution problems.

Blast Furnace Smelting Process (6). Semisoft/hard lead which is a product and an intermediate product, is produced from pretreated scrap, antimonical slag (reverberatory slag), and rerun slag by the blast furnace smelting process. In this process the molten lead flows almost continuously and the slag is tapped at intervals. A typical charge which is added as the material melts down is: 4.5 percent scrap iron; 3 percent limestone; 5.5 percent coke; and 82.5 percent drosses, oxides, and reverberatory slag. The drosses are miscellaneous drosses consisting of copper drosses, caustic dross, and dry drosses from the refining process in the pot furnace. Thus, the process steps are: (a) add the charge with a composition as noted above, (b) continuously remove the molten lead, (c) remove the slag at intervals, and (d) cast the lead ingots or transfer molten lead to the refining kettles.

The energy utilized in this process is from coke, which also serves as a reducing agent.

Waste products produced by this process are atmospheric emissions and solid wastes. The atmospheric emissions consist of gases containing carbon monoxide, hydrocarbons, sulfur oxides, nitrogen oxides, and probably

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(7) Nance, J. T., and K. O., Luedtke, Lead Refining, Air Pollution Engineering Manual, Danielson, J. A. (ed), U. S. DHEW, PHS, National Center for Air Pollution Control, Cincinnati, Ohio, Pub. No. 999-AP-40, pp 300-304 (1967).

(8) Allen, G. L., et al., Control of Metallurgical and Mineral Dusts and Fumes in Los Angeles County, Dept. of the Interior, Bureau of Mines, Washington, D. C., Information Circular No. 7627, April, 1952.

(9) Hammond, W. F., Data on Nonferrous Metallurgical Operations, Los Angeles County Air Pollution Control District, November, 1966.

(10) Unpublished work, Battelle's Columbus Laboratories (1972).

nitrogen. The particulate matter in the emissions contains oil vapor, smoke, fume, and dust. The fume and dust are composed of lead, tin, zinc, coke dust, sulfur, and other metals contained in the charge. The fumes are volatized and condensed from the charge, whereas the dusts are carried from the furnace by entrainment in the furnace gases.

Particle morphology of the particulate emissions are similar to those from the reverberatory furnace. Particle size ranges from 0 to 16 microns with approximately 15 percent between 0 to 1 micron, 45 percent between 1 to 2 microns, 20 percent between 2 to 3 microns, 15 percent between 3 to 4 microns, and 10 percent between 4 to 16 microns(11). No data are available on particle shape; however, the dust is most likely irregular and the fume (smaller size) is spherical.

Emissions rate is high from the blast furnace smelting process. Raw particulate emissions factor (uncontrolled) is estimated at 190 lb per ton of metal processed. Sulfur oxide emissions factor is estimated at 90 lb per ton of metal processed.(12) Controlled emissions factors are 2.3 and 0.8 to 46 lb per ton of metal processed, respectively.

The emissions are subject to control. The baghouse is the most acceptable device for controlling the particulate emissions. The gas stream containing the emissions is first passed through a series of water or air cooled tubes and then to the baghouse. To prevent tar volatiles from blinding the bags, the temperature of the baghouse is kept high. Lime is also added to the gas stream to prevent the blinding action. The gas stream from the baghouse is discharged to a stack or possibly to an electrostatic precipitator in an attempt to further clean the gases before emitting them to the atmosphere.(13)

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(11) Air Pollution Engineering Manual, U. S. Dept. HEW, NCAPC, Cincinnati, Ohio, p 303 (1967).

(12) Compilation of Air Pollutants Emission Factors, 2nd Ed., U. S. EPA, Office of Air and Water Programs, Research Triangle Park, North Carolina, p 7.11-2 (April, 1973).

(13) U. S. Dept. of Commerce, Economic Impact of Air Pollution Controls on the Secondary Nonferrous Metals Industry, Washington, D. C., p 132 (1969).

Wet scrubbers may be employed to clean the gaseous portion of the stream. The caustic (NaOH) scrubber is more effective than the water spray chamber for removing sulfur oxides as evidenced by the fact that caustic scrubbing reduced the emissions factor from 90 lb per ton of metal processed to 0.8 lb per ton of metal processed, whereas water scrubbing reduced the emission factor to only 46 lb per ton of metal processed.(14)

Solid wastes from this process are the baghouse and flue dusts and fumes, and the slag. For the most part, these are recycled to the process because of the high lead content.

Thus, uncontrolled, the blast furnacing process produces large quantities of atmospheric emissions and solid wastes which can cause serious pollution problems, both from the atmospheric and water pollution aspects.

Refining/Casting Operation

The intermediate products from the reverberatory and blast furnace processes--soft lead and antimonical lead--required additional purification or refining to produce the desired products. In addition to the metal products, some of the lead is converted to lead oxide products. The processes employed to achieve conversion of the impure lead intermediate products to the final products are processes 7 through 11 as shown in the attached flowsheet.

Kettle (Softening) Refining Process (7).

The intermediate products from the smelting operation may contain copper (generally not present) and antimony which makes the lead hard. Removal of these two contaminants by the kettle (softening) refining process produces soft lead--one of the products from the lead segment of secondary nonferrous metals industry. The process steps are: (a) charge the preheated kettle, (b) melt the charge, (c) stir the molten charge to mix in the flux, (d) remove the skimmings, (e) pour the molten metal, and (f) cast into ingots (bullion). In some cases, the molten lead is poured directly from the smelting operation to the refining kettle.

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(14) Compilation of Air Pollutant Emission Factors, 2nd Ed., U. S. EPA, Research Triangle Park, North Carolina, p 7.11-2 (April, 1973).

Several fluxes or purifiers are used. Included in this list are sodium hydroxide, sodium nitrate, aluminum chloride, or aluminum. Air is occasionally used to blow the melt.

Source of energy for this process is generally gas to heat the kettle indirectly and electricity to drive the equipment.

Waste products produced are atmospheric emissions and solid wastes (skimmings). The atmospheric emissions containing mainly fumes and possibly some dust are composed of such metals as lead, antimony, sodium, and trace quantities of copper, zinc, arsenic, bismuth, and tin. The gaseous portion of the emissions contains primarily the fuel combustion gases.

Particle morphology should be similar to the fumes from the reverberatory smelting process, i.e., the particle size is in the submicron range and the shape is generally spherical.

Although the quantity of emissions from the refining process is much less than from the other lead processes, for example, 0.8 lb of particulates per ton of metal processed as compared to 190 lb per ton of metal processed for reverberatory smelting, the toxic or hazardous nature of lead requires that the emissions be controlled. The most widely used device is the baghouse. The fumes are collected via a hood over the kettle.(15)

The solid wastes are skimmings containing the flux and other metal values removed from the melt during the refining operation. These wastes along with the particulate matter from the baghouse are generally recycled to the blast furnace for recovery of the lead value.

Thus, the kettle (softening) refining process produces waste products which can cause pollution problems, if wastes are not collected and disposed of in a nonpolluting manner.

Kettle (Alloy) Refining Process (8). Kettle (alloy) refining process involves treatment and adjustment of the metals content of lead to produce the desired lead alloy. This involves the following process steps: (a) charging the preheated kettle, (b) melting the charge, if not added molten, (c) stirring to mix the flux into the charge, (d) skimming to remove collected impurities, (e) pouring, and (f) casting. Alloying agents commonly used are antimony, copper, silver, and tin.

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(15) Blythe, D. J., Ed., "Lead and Arsenic Reports", Journal of the Air Pollution Control Association, 10 (5), p 940-944 (1955).

Source of energy for this process is natural gas and electricity to drive the equipment.

Emissions data--waste products produced, emissions factor, control of emissions, and particle morphology--are essentially the same for this process as for Process 7.

Thus, the process can be a source of environmental pollution.

Kettle Oxidation Process (9). Battery lead oxide (PbO containing approximately 20 percent lead metal) is produced by the kettle oxidation process. The process steps are: (a) charge kettle with molten lead from a melting pot, (b) rapidly agitate (mechanically) the lead, (c) draw air over the surface of the melt through the duct leading to the baghouse, and (d) collect the lead oxide (fumed from the surface of the melt) in the baghouse.

Source of energy is natural gas to heat the melt furnace and the oxidation furnace, and electricity to drive the equipment.

Atmospheric emissions are produced by this process. These include (1) the combustion gases which are separate from those from the melting chamber, oxidation chamber, and the baghouse; and (2) fumes and dust from the melting and oxidation chambers and the baghouse. The gases are composed of carbon dioxide, carbon monoxide, sulfur oxides, nitrogen oxides, and unburned fuel, whereas the particulate matter contains lead oxide, lead metal, and other metal values from the melting and oxidation chambers and the baghouse.

The major source of emissions is the baghouse since the air is being swept over the oxidation chamber into the baghouse. Emission factor for the baghouse will vary somewhat, but in most oxide collection systems, collection efficiency averages greater than 98 percent. On this basis, emissions factor is estimated at less than 40 lb of lead oxide per ton of oxide produced. Particle size of the oxide is in the submicron range (approximately 0.2 to 0.5 micron) and particle shape is spherical.

Thus, the kettle oxidation process is a source of pollution problems.

Reverberatory Oxidation Process (10). The most widely used lead oxide pigments are lead monoxide (PbO) and red lead (Pb_3O_4). These are produced by the reverberatory oxidation process. The process steps are: (a) charge the hot reverberatory furnace with molten lead, (b) agitate the melt while oxidizing the lead to lead oxide, and (c) remove the lead oxide from the furnace and cool rapidly. Lead oxide (PbO) is produced by fully oxidizing the lead, whereas red lead (Pb_3O_4) is produced by over-oxidizing the PbO.

Energy required for this process is from the fuel (natural gas or fuel oil) to heat the furnace.

Waste products produced by this process are atmospheric emissions. These emissions are gases containing the combustion gases, excess air, and nitrogen and particulate matter containing lead oxide along with the impurities found in the lead charge. These emissions are carried from the furnace by entrainment in the furnace gases or from volatilization and condensation of the lead oxide fumes. Particle size is in the submicron range and the particles are spherical in shape.

Emissions data are not available for the reverberatory oxidation process. However, it is estimated that the emission factor will range from approximately 40 to 150 lb per ton of lead oxide produced. These emissions are most likely controlled by a baghouse.

Thus, the reverberatory oxidation process for producing lead oxides can be a source of serious pollution problems.

Population of Secondary Lead Processors

(1) Abrams Waste Materials Company
1421 S. McBride Street
Syracuse, New York

(2) Allie Smelting Corporation
5116 W. Lincoln Avenue
Milwaukee, Wisconsin 53219
Telephone: (414) 541-7830

(3) Cambridge Smelting Company
100 Pacific Street
Cambridge, Massachusetts

(4) Chicago Smelting and Refining Co.
3701 S. Kedzie Avenue
Chicago, Illinois

(5) Colinial Metals Company
Columbia, Pennsylvania
Telephone: (717) 684-2311

(6) Crown Metal Company
123 E. Washington
Milwaukee, Wisconsin

(7) Detroit Lead Pipe Works, Inc.
1701 Linden Avenue
Detroit, Michigan

(8) Electric Storage Battery Company
2 Penn Central Plaza
Philadelphia, Pennsylvania
Telephone: (215) 564-4030

(9) Florida Smelting Company
2640 Capitola Street
Jacksonville, Florida
Telephone: (904) 353-4317

(10) General Battery and Ceramic Corporation
Post Office Box 1262
Reading, Pennsylvania

(11) Industrial Metal Smelting Co.
1508 Open Street
Baltimore, Maryland

(12) Industrial Smelting Company
19430 Mt. Elliott & Marx Sts.
Detroit, Michigan

(13) Inland Metals Refining Company
651 E. 119th Street
Chicago, Illinois 60628

(14) Lead Products, Inc.
Manchester, Connecticut

(15) Nassau Smelting and Refining Company, Inc.
5 Nassau Place
Tottenville, New York
Telephone (212) 984-1970

(16) National Lead Company
111 Broadway
New York, New York 10006
Telephone: (212) 732-9400

(17) North American Smelting Company
Terminal (P. O. Box 1952)
Wilmington, Delaware
Telephone: (302) 654-9901

(18) Price Battery Corporation
942 Grand Street
Hamburg, Pennsylvania

(19) Rochester Lead Works, Inc.
Exchange and Ewell Sts.
Rochester, New York

(20) Schuylkill Products Co, Inc.
Post Office Box 3916
Baton Rouge, Louisiana
Telephone: (504) 775-3040

(21) Seitzinger's Inc.
Post Office Box 1336
Atlanta, Georgia
Telephone: (404) 876-3787

(22) Southern Lead Company
2823 NW Moreland Road
Post Office Box 6195
Dallas, Texas
Telephone: (214) 331-3241

(23) U. S. Smelting Works
American and Bristol Streets
Philadelphia, Pennsylvania

(24) U. S. Lead Refinery, Inc.
5300 Kennedy Avenue
East Chicago, Indiana
Telephone: (219) 397-1012

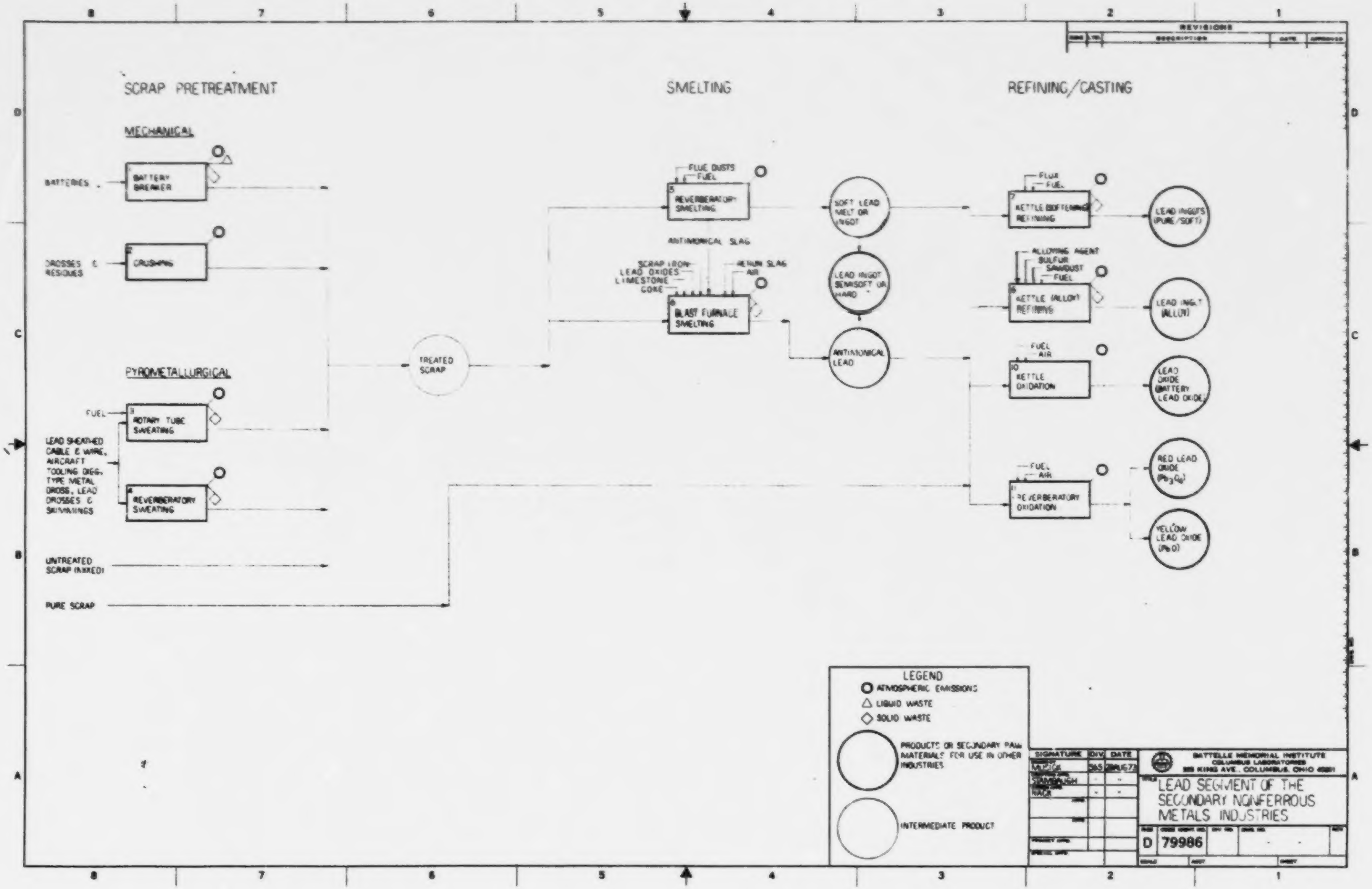
(25) Hyman Viener & Sons
Richmond, Virginia 23205
Telephone: (703) 648-6563

(26) Wenesley Metal Products Company
1415 Osage
Denver, Colorado

(27) Western Lead Parts Company
City of Industry, California

(28) Willard Smelting Company
101 E. New Bern
Charlotte, North Carolina

(29) Winston Lead Smelting Company
Winston-Salem, North Carolina


SCRAP PRETREATMENT
MECHANICAL
BATTERIES
1 BATTERY BREAKER
DROSSES & RESIDUES
2 CRUSHING
PYROMETALLURGICAL
FUEL
3 ROTARY TUBE SWEATING
LEAD SHEATHED CABLE & WIRE, AIRCRAFT TOOLING DIES, TYPE METAL DROSS, LEAD DROSSES & SKIMMINGS
4 REVERBERATORY SWEATING
UNTREATED SCRAP (MIXED)
PURE SCRAP
TREATED SCRAP
SMELTING
FLUE DUSTS
FUEL
5 REVERBERATORY SMELTING
ANTIMONICAL SLAG
SCRAP IRON
LEAD OXIDES
LIMESTONE
COKE
RERUN SLAG
AIR
6 BLAST FURNACE SMELTING
SOFT LEAD MELT OR INGOT
LEAD INGOT SEMISOFT OR HARD
ANTIMONICAL LEAD
REFINING/CASTING
FLUX
FUEL
7 KETTLE (SOFTENING) REFINING
LEAD INGOTS (PURE/SOFT)
ALLOYING AGENT
SULFUR
SAWDUST
FUEL
8 KETTLE (ALLOY) REFINING
LEAD INGOT (ALLOY)
FUEL
AIR
10 KETTLE OXIDATION
LEAD OXIDE (BATTERY LEAD OXIDE)
FUEL
AIR
11 REVERBERATORY OXIDATION
RED LEAD OXIDE (Pb3O4)
YELLOW LEAD OXIDE (PbO)
LEGEND
○ ATMOSPHERIC EMISSIONS
△ LIQUID WASTE
◇ SOLID WASTE
PRODUCTS OR SECONDARY RAW MATERIALS FOR USE IN OTHER INDUSTRIES
INTERMEDIATE PRODUCT
REVISIONS
DESCRIPTION
DATE
APPROVED
SIGNATURE
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MUSICK
565
29AUG72
STAMBAUGH
HACK
BATTELLE MEMORIAL INSTITUTE
COLUMBUS LABORATORIES
505 KING AVE., COLUMBUS, OHIO 43201
LEAD SEGMENT OF THE SECONDARY NONFERROUS METALS INDUSTRIES
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PROCESS DESCRIPTION OF THE MAGNESIUM SEGMENT OF SECONDARY NONFERROUS METALS INDUSTRY

Magnesium recovered from scrap constitutes approximately 10 percent of the U. S. production of magnesium metal. In 1972, this amounted to 15,662 short tons,(1) most of which was recovered from aluminum alloys. Emissions from the magnesium segment include minor amounts of particulates and gases emitted to the atmosphere and solid waste to the land.

Raw Materials

Major sources of raw material to this segment include new scrap (79 percent) and old scrap (21 percent). Most of the new scrap comprises magnesium-aluminum alloys generated in-house in the fabrication and machining of finished components. The old scrap, also comprised of magnesium-aluminum alloys, is generated from scrap automobile and aircraft parts and, therefore, contains hand sortable ferrous and nonferrous metallic parts. Other sources of scrap include drosses and sludges.

Products

Products from the magnesium segment of the secondary nonferrous metals industry include:

(1) Magnesium alloy ingot
(2) Magnesium alloy castings and shapes
(3) Aluminum-magnesium alloys
(4) Zinc and other alloys
(5) Cathodic protection rods.

Items (1), (3), and (5) constitute more than 90 percent of the products.

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(1) Telephone conversation with E. Chin, Chemist, Division of Nonferrous Metals, USBM, Washington, D. C.

Process Description

The recovery of magnesium from scrap involves three manufacturing operations: (1) scrap pretreatment, (2) smelting, and (3) casting. These operations and the individual processes under each operation are shown in the flowsheet entitled "Magnesium Segment of The Secondary Nonferrous Metals Industry"

Scrap Pretreatment Operation

Magnesium scrap is hand sorted to separate the large and easily identifiable pieces of other metals from the scrap magnesium parts as shown in the flowsheet and discussed below.

Hand Sorting Process (1). The process consists of separating the magnesium and magnesium-alloy parts from all the other metals present in the scrap. The processing steps involve (1) spreading the scrap on the floor and (2) hand picking the lightest pieces which are magnesium and magnesium-alloys. This hand picking of light metal becomes second nature to the person experienced in the process.

The process does not require any energy except human labor.

Fine particles left on the floor constitute the solid waste generated by this process. It is usually insignificant as a source of pollution. Thus, the hand sorting process does not offer any potential for pollution.

Smelting Operation

The smelting of sorted scrap magnesium and the smelting of drosses and sludges are the two processes under this operation. However, the same company does not necessarily do both these operations. The scrap melting facility finds it convenient to ship its sludge (slag) to a sludge processing facility, thus avoiding a potential solid waste disposal problem at the scrap melting plant.

Open Pot Melting Process (2). The sorted solid magnesium and alloy scrap is transferred to a melt crucible of about 1000-lb capacity, where the scrap is melted and the magnesium separated from the contaminants. The process steps are: (1) heat the crucible to melt the scrap, (2) add flux which is a mixture of calcium, sodium, and potassium chlorides, (3) pour the molten metal into molds, (4) cast the ingots, and (5) remove the slag or sludge.

Thermal energy is the main energy requirement of this process.

The wastes generated are: (1) gaseous effluents consisting of chlorine, hydrogen chloride, smoke from oil and grease, and particles of dust, including small amounts of magnesium oxide (MgO); and (2) solid waste as sludge containing slag which is sent for reprocessing at a sludge smelter. The estimated uncontrolled particulate emission factor for a pot furnace is 4 lb per ton of metal processed.(2)

This process has a moderate air pollution problem arising from the gases generated. In fact, the in-house pollution is a greater threat to the plant personnel than it is to the public by way of ambient air pollution. Some installations use hoods to vent the gases to ambient air.

The potential pollution from this process is significant by way of air pollution if not controlled properly.

Sludge Smelting Process (3). This process recovers magnesium from sludges produced in primary and secondary smelters. The process steps are: (1) heating, (2) flux addition, (3) slag removal, and (4) casting.

Energy required for this process is thermal energy.

Potential pollutants from this process are solid wastes and atmospheric emissions. The solid waste--slag--contains the fluxes and contaminants removed from the scrap. The atmospheric emissions are composed of chlorine and hydrogen chloride gases from the melting pot, combustion gases, and dust.

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(2) USEPA, "Compilation of Air Pollution Emission Factors", Publication AP-42, USEPA, Washington, D. C. (April, 1973).

The atmospheric emissions, if uncontrolled, present an atmospheric pollution problem, while the slags are a source of water pollution if disposed of in an unapproved landfill.

Casting Operation

Ingot Casting Process (4). The molten magnesium is cast into ingots in this process. The process steps are: (1) covering the melt with a protective flux, (2) pouring the melt into casting dies, and (3) casting the melt.

Energy requirements of this process are not significant.

Minor quantities of atmospheric emissions are generated. Thus, the quantity of emission is too small to represent any pollution potential.

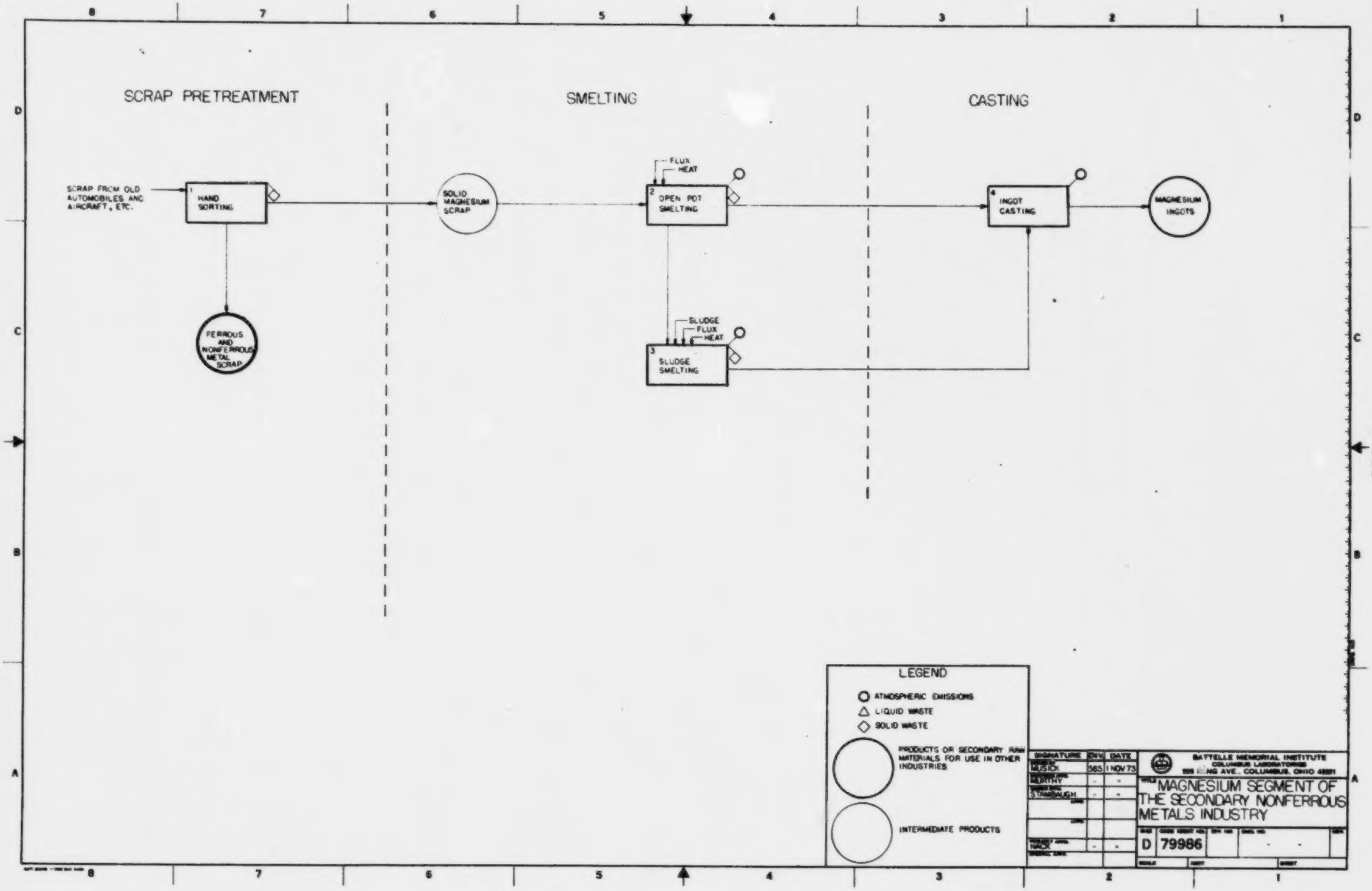
Population of Secondary Magnesium Processors

(1) American Smelting and Refining Company
Federated Metals Division
12 Pine Street
New York, New York

(2) Apex Smelting Company
Division of Amax Aluminum Company
2515 West Taylor Street
Chicago, Illinois
Telephone: (312) 332-2214

(3) Standard Magnesium
Division of Kaiser Chemicals
41st and Memorial Drive
Tulsa, Oklahoma

(4) White Metal Rolling and Stamping Corporation
84 Moultrie Street
Brooklyn, New York


SCRAP PRETREATMENT
SMELTING
CASTING
SCRAP FROM OLD AUTOMOBILES AND AIRCRAFT, ETC.
1 HAND SORTING
FERROUS AND NONFERROUS METAL SCRAP
SOLID MAGNESIUM SCRAP
FLUX
HEAT
2 OPEN POT SMELTING
SLUDGE
FLUX
HEAT
3 SLUDGE SMELTING
4 INGOT CASTING
MAGNESIUM INGOTS
LEGEND
○ ATMOSPHERIC EMISSIONS
△ LIQUID WASTE
◇ SOLID WASTE
PRODUCTS OR SECONDARY RAW MATERIALS FOR USE IN OTHER INDUSTRIES
INTERMEDIATE PRODUCTS
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STAMBAUGH
HACK
BATTELLE MEMORIAL INSTITUTE
COLUMBUS LABORATORIES
505 KING AVE., COLUMBUS, OHIO 43201
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MAGNESIUM SEGMENT OF THE SECONDARY NONFERROUS METALS INDUSTRY

PROCESS DESCRIPTION OF THE MERCURY SEGMENT OF THE SECONDARY NONFERROUS METALS INDUSTRY

The U. S. production of mercury by secondary recovery processes was 12,139 flasks(1) in 1972, representing 62 percent of all mercury produced in the U. S. in that year. The salient statistics on the consumption and production of mercury for the preceding two years are as follows.(2)

	1971	1972
Domestic consumption--flasks	52,275	52,907
Production, primary processing	17,883	7,286
secondary processing	10,899	12,139
Imports (for consumption)	28,449	28,834

The data indicate a sharp rise in mercury production by this segment while production from the primary industry declined sharply, probably due to a decrease in demand caused by the stringent mercury emission standards(3) in December, 1971.

Emissions to the land, water, or air from secondary mercury processing, quantitatively speaking, are not significant. However, the extreme toxicity of the mercury vapor makes a careful study of this industry worthwhile. Due to the relatively high vapor pressure of mercury, ambient mercury concentrations around open vessels can be sufficiently greater than the threshold limit value (TLV) even at ordinary pressure and temperature. If good housekeeping in the secondary processing plants is insured, mercury pollution will not reach significant levels. The flowsheet on the mercury segment of the Secondary Nonferrous Metals Industry provides a flow of the processes and potential sources of emissions from each of the processes.

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(1) Flask as used throughout this segment report refers to the 76-lb flask.

(2) Telephone conversation with V. Anthony Cammarota, Jr., Mercury Specialist, USBM, Washington, D. C.

(3) Federal Register, National Emissions Standards for Hazardous Air Pollutants, Vol. 36, No. 234, pp 23,239-23,256 (December, 1971).

Raw Materials

Reported high volume sources of scrap for reprocessing include the following:

(1) Salvage from instrument and electrical manufacturers, research laboratories (dirty liquid mercury from research organizations, educational institutions, etc.)

(2) Mercury battery scrap

(3) Industrial scrap

(4) Dental amalgam.

The most common single source mentioned is dental amalgam, though the absolute volume of this source is relatively small. Obviously, in this case, silver, rather than mercury, provides the primary incentive for recovery.(4)

Federal Effluent Standards for water considered to be in the making may have created another source of scrap mercury. The chlor-alkali plant liquid effluent contains about 20 ppm mercury which needs to be reduced to less than 5 parts per billion (ppb) which is considered to be the level of mercury allowable by the regulations. Rosenzweig(5) outlines the flow schemes of two processes for mercury recovery from wastewater. One of them, the Osaka Soda Process, generates a resin as a solid waste containing small amounts of recoverable mercury. The solid waste generated is not significant (about 1000 lb per year). Also, the amount of mercury recovered by these processes is not significant enough to warrant further study as a scrap recovery system.

Product

The product from the mercury segment of the secondary metals industry is liquid mercury.

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(4) ORNL Report, "Survey of the Mercury Reprocessing Industry 1968-1970", Report No. NSF-EP-22, ORNL, Oak Ridge, Tennessee 37830 (October, 1972).

(5) Rosenzweig, Mark D., "Pairing Mercury Pollution", Chemical Engineering, pp 70-71, February 22, 1971.

Process Description

The recovery of mercury from scrap involves three manufacturing operations: scrap pretreatment, refining, and bottling. These operations and the individual processes under each operation are shown on the flowsheet entitled "Mercury Segment of the Secondary Nonferrous Metals Industry".

Scrap Pretreatment Operation

There is no pretreatment of the scrap when vacuum distillation is employed as the refining method. The dirty liquid mercury scrap is fed directly to the distillation vessel. However, during transfer of the scrap mercury from the storage to the distillation flask, a small quantity of mercury may escape as vapor. This does not constitute any potential for widespread pollution. Building ventilation at the plant is sufficient to reduce the mercury levels to below the OSHA's TLV of 100 $\mu g/m^3$ (Federal Register, Vol. 37, No. 202, October 18, 1972).

Prefiltration Process (1). This is a pretreatment operation used only with the oxygenation process and when the mercury scrap contains insoluble impurities that need to be removed before oxygenation starts. In fact, this is the only scrap pretreatment operation in the entire secondary mercury industry. The process removes insoluble impurities by filtering which is a single process step.

Energy, mostly electrical, is required for the filtration process.

The solid waste (dirt) generated is sent to the retorting process for recovery of trace amounts of mercury that may be present.

The prefiltration process presents no potential serious pollution problem providing the area is vented and gases are cleaned prior to emitting to the atmosphere.

Refining Operation

There are four different processes used for refining scrap mercury. The process employed depends on the type of scrap. Each of the processes (2 through 5) is shown in the flowsheet on the mercury segment and discussed below.

Vacuum Distillation Process (2). When the vapor pressure of the impurities is substantially lower than that of mercury, purification by vacuum distillation which separates a high purity mercury from the impurities is employed. The distillation unit consists of a still pot for heating the impure mercury, a water cooled condenser, and a pure mercury receiving vessel. The processing steps are: (1) heating the still pot by external heat to vaporize the mercury at an absolute pressure of 0.01 torr (0.01 mm Hg Pressure), (2) condensing the mercury in water-cooled condensers, and (3) collecting the clean mercury in a receiver. Afterwards, the still residue is removed for further processing.

Energy requirements for this operation are: (1) heat energy for heating the distillation still and (2) electrical energy to operate the vacuum pump and associated equipment.

The main source of potential pollution is the exhaust gas from the vacuum pump. Estimated maximum mercury emissions(6) by distillation are 0.02 lb per 760 lb of mercury produced. Solid waste residue from the still pot is normally recycled to other refining processes. No liquid effluent is produced in this process.

The process has no serious pollution potential if good housekeeping practices are employed and precautions are taken to control emissions.

Solution Purification Process (3). This process removes metallic and/or organic impurities contained in the dirty liquid mercury by washing with a dilute acid. The processing steps are (1) leaching metallic impurities with dilute nitric acid using compressed air to mix the acid and mercury; (2) separating the mercury layer from the aqueous nitric acid slurry by decantation; (3) water washing to remove residual acid, and (4) filtering, probably through a bed of activated charcoal and silica gel, to remove last traces of water. If the mercury contains organic impurities, the scrap mercury is treated in the same manner with organic solvents.

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(6) Battelle's Columbus Laboratories report to EPA, "Topical Report on Basis for National Emission Standards on Mercury", Battelle's Columbus Labs, Columbus, Ohio, June 15, 1971.

Electrical energy is required to operate the compressor and associated equipment. Pumping the mercury is avoided by use of gravity flow scheme from overhead tanks.

Potential pollutants generated by this process are atmospheric emissions, liquid wastes, and solid wastes.

The atmospheric emissions containing mercury vapor result from sparging of the liquid mercury during the leaching step. The spent leach liquor is the source of liquid waste, while the solid waste consists of the contaminated filter media.

In view of the hazardous nature of mercury, pollution problems can result.

Oxygenation Process (4). This process, also called oxification, removes the metallic impurities contained in dirty liquid mercury by oxidation with sparging air. The process steps are: (1) sparging the dirty mercury with air in a closed, agitated vessel for several hours and (2) filtration to remove solid metal oxides. Finally, the filtered mercury is bottled which is discussed in the bottling process.

Electrical energy is required for sparging and water scrubbing process steps.

Sparging air which contains saturation levels of mercury at 77 F is a potential atmospheric pollutant. However, before venting to the atmosphere, it is generally water scrubbed and filtered through a bed of charcoal to remove the mercury. The water is recycled many times before discharge because mercury settles out of the water. In most cases, the solid waste as filter cake is sent to the retorting process. Thus, the potential pollutants from this process are atmospheric emissions, liquid wastes, and solid wastes.

The potential for pollution from this process is not significant, providing pollutants are treated before discharging to the environment.

Retorting Process (5). This process produces pure mercury by volatilization of the mercury contained in solid scrap. Examples of scrap are dental amalgams, mercury battery scrap, and distillation sludges. The process steps are: (1) external heating of solid scrap in a closed still pot or stack of trays to volatize the mercury, (2) cooling mercury vapor in water-cooled condensers to condense the vapors, and (3) bottling which is discussed in Process (6).

Heat energy is required for volatilization of mercury and electrical energy for cooling water circulation.

Potential pollutants generated by the process are atmospheric emissions from the retort, liquid wastes from the condenser, and cleaning of the atmospheric emissions and solid wastes as the retort residue, each containing mercury. The degree of pollution can be reduced by scrubbing of the process gases prior to emission to the atmosphere, packaging of the retort residue and disposing of it in a hazardous landfill, and treating the liquid wastes prior to disposal.

Because of the hazardous nature of mercury, this process can be a source of serious pollution problems.

Bottling Operation

Bottling Process (6). Bottling of the purified mercury is done to enable marketing of the product in 76-lb flasks.

The steps are (1) pumping or manual pouring of the mercury into the 76-lb bottles and (2) sealing the bottling.

Electrical energy is used for pumping the mercury to the bottles.

The only waste emission is mercury vapor (at 77 F), produced when pumping or pouring mercury into the bottle. This is not a significant source of air pollution but can cause high levels of mercury vapor inplant. Building ventilation air is used to reduce the mercury levels to below the TLV.

The bottling process does not offer any potential for serious air pollution.

Population of Secondary Mercury Processors

(1) Florida Smelting Company
2640 Capitola Street
P. Box 3404
Jacksonville, Florida
Telephone: (904) 353-9317

(2) Kahl Scientific Instrument Corporation
737 West Main Street
El Cajon, California 92022
Telephone: (714) 444-5944

(3) Metallurgical Products Company
35th and Moore Streets
Philadelphia, Pennsylvania 19148
Telephone: (215) 394-8300

(4) Wood-Ridge Chemical Corporation
Park Place East
Wood-Ridge, New Jersey 07075
Telephone: (201) 939-4600

(5) Eastern Smelting and Refining Corporation
35 Bubier Street
Lynn, Massachusetts 01901

(6) Martin Metals, Inc.
1321 Wilson Street
Los Angeles, California 90021

(7) Mallory (P.R.) and Company, Inc.
3029 East Washington Street
Indianapolis, Indiana 46206

(8) Bethlehem Apparatus, Inc.
890 Front Street
Hellerton, Pennsylvania 18055

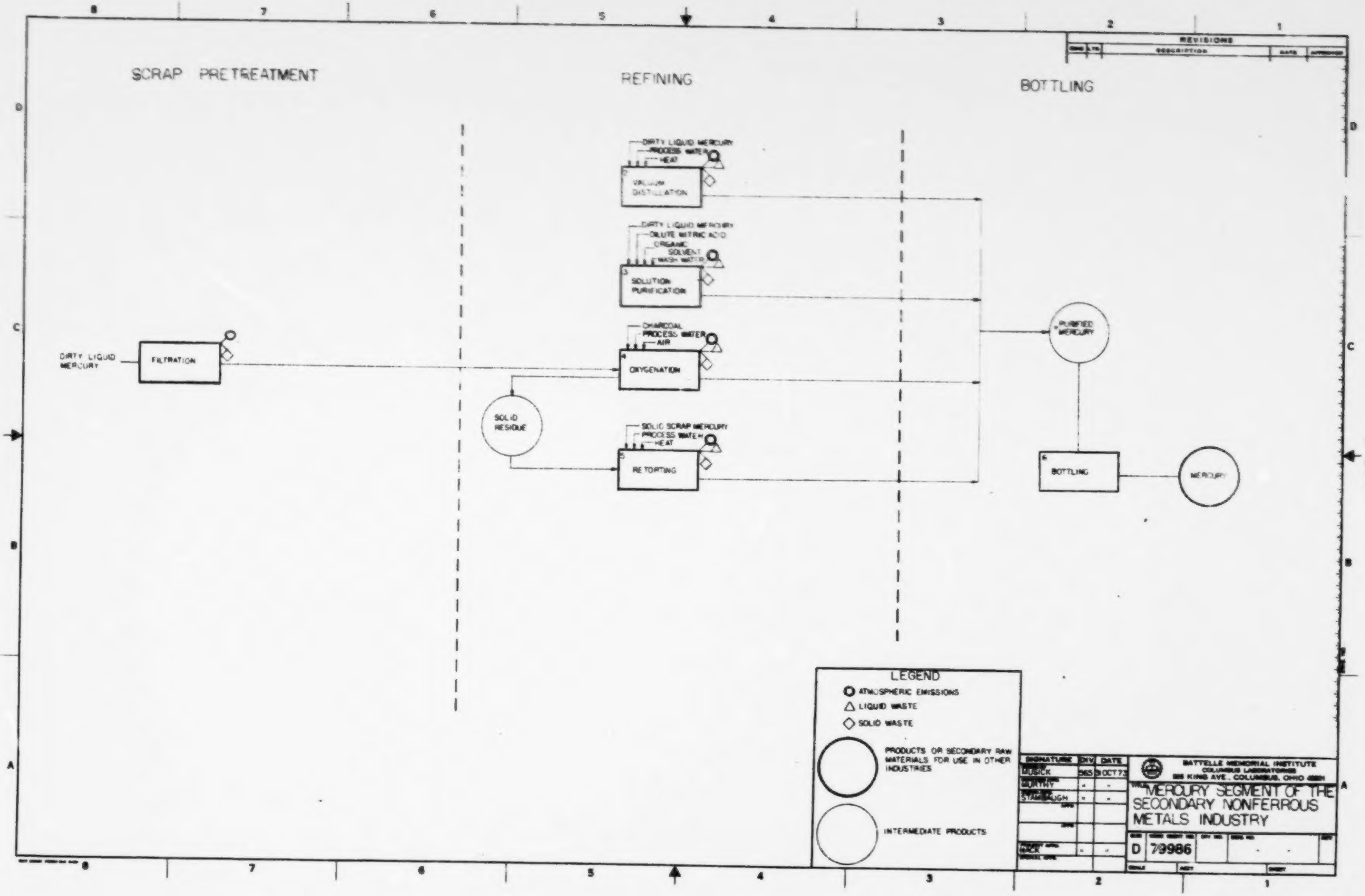
(9) Dresher Metal Trading, Inc.
Box 44
Dresher, Pennsylvania 19025

(10) D. F. Goldsmith Chemical and Metal Corporation
109 Pither Avenue
Evanston, Illinois 60202

(11) Williams Gold Refining, Inc.
2978 Main Street
Buffalo, New York 14214

(12) Merck and Company
Metal Salts Division
Hawthorne, New Jersey

(13) Iritox Chemical Company
284 Hamilton Avenue
Brooklyn, New York 11231


SCRAP PRETREATMENT
REFINING
BOTTLING
DIRTY LIQUID MERCURY
FILTRATION
DIRTY LIQUID MERCURY
PROCESS WATER
HEAT
2 VACUUM DISTILLATION
DIRTY LIQUID MERCURY
DILUTE NITRIC ACID
ORGANIC SOLVENT
WASH WATER
3 SOLUTION PURIFICATION
CHARCOAL
PROCESS WATER
AIR
4 OXYGENATION
SOLID RESIDUE
SOLID SCRAP MERCURY
PROCESS WATER
HEAT
5 RETORTING
PURIFIED MERCURY
6 BOTTLING
MERCURY
LEGEND
ATMOSPHERIC EMISSIONS
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BATTELLE MEMORIAL INSTITUTE
COLUMBUS LABORATORIES
505 KING AVE., COLUMBUS, OHIO 43201
MERCURY SEGMENT OF THE SECONDARY NONFERROUS METALS INDUSTRY
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PROCESS DESCRIPTION OF THE NICKEL SEGMENT OF THE SECONDARY NONFERROUS METALS INDUSTRY

During 1971, this segment recovered 29,657 short tons of nickel, mostly as alloys, from old and new scrap. This recovery amounted to about 30 percent of total U. S. nickel consumption. It is estimated* that only about 40 percent of the available scrap is recycled. The remaining 60 percent, such as used nickel-cadmium batteries and spent nickel-base catalysts, are disposed of in landfills. Emissions to the environment from this segment are atmospheric emissions and solid wastes.

Raw Materials

Raw materials include old scrap (74 percent) and new scrap (26 percent) both comprising of nickel-, copper-, and aluminum-base alloys. The scrap originates as used burners (inconel), airplane parts, sheet scrap, electrical scrap, and so on. An exact percent breakdown of the contribution of these sources is not available.

Products

Products from the nickel segment are slag and the following alloys:

(1) Stainless steels (18/8 and other grades)
(2) Nickel-base alloys (cupronickel, nickel silver, etc.)
(3) Base alloys (low alloy steels)
(4) Nickel metal (quantitatively not significant).

Process Description

The recovery of nickel as nickel alloys from scrap involves three manufacturing operations: (1) scrap pretreatment, (2) smelting, and (3) refining/casting. These operations and the individual processes under each operation are shown in the flowsheet entitled "Nickel Segment of The Secondary Nonferrous Metals Industry".

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(1) Battelle's NASMI Report, "A Study to Identify Increased Solid Waste Utilization", Battelle's Columbus Laboratories, Columbus, Ohio 43201, (June, 1972).

Scrap Pretreatment Operation

Hand Sorting Process (1). This process is done usually at the scrap merchant's facilities rather than at the scrap smelting facilities.

The process segregates the nickel bearing alloys and metals from the nickel-free components in the raw scrap.

The process steps are: (a) spread the scrap on a platform and (b) separate the nickel scrap from the nonmetallics and nonnickel components.

Manual labor is the only energy requirement for the process.

Wastes produced are limited to a small quantity of solid wastes which are composed of dirt and nonnickel scrap.

The pollution potential of the waste is insignificant.

Smelting Operation

In the smelting operation, partial purification of the nickel scrap is achieved or the nickel scrap is melted and mixed with selected alloying agents as outlined in the segment flowsheet by Processes 2 and 3.

Electric Arc Process (2). This process produces a partially purified product which is purified further in the refining/casting operation or nickel alloys which are cast into alloy ingots.

The process steps are: (a) charging the scrap to the electric arc furnace, (b) adding a reductant (lime), (c) melting the charge, (d) pouring into molds or transferring the molten metal to a reactor for refining, and (e) removing the slag.

Electric energy is required in substantial quantities for this process to operate the furnace. Additional energy is required to operate the auxiliary equipment.

Wastes generated are: (1) atmospheric emissions consisting of large quantities of dust particles and limited quantities of gases and (2) solid wastes consisting of furnace slag.

The off gases are invariably treated in a baghouse which removes approximately 99 percent of the dust particles. Hence, the gases are clean when vented and do not constitute any serious air pollution problem. However, the collected dust (about 4 tons/day at a medium size facility) is sent to a landfill and may be considered a potential source of water pollution by leaching to surface and ground waters. The metal value of this dust is unknown and the industry would like to investigate possibilities of recovery of any metals in the dust.*

The slag may or may not be a waste as, in many cases, it is ground at another facility for use in sandblasting or road surfacing operations.*

Rotary Reverberatory Furnace Smelting Process (3). This process is the same as Process (2) except a reverberatory furnace is used in place of an electric arc furnace. The process steps are: (a) charging the scrap to the furnace, (b) adding a reductant (lime), (c) melting the charge, (d) pouring the melt in the molds or transferring the melt to a reactor for refining, and (e) removing the slag.

Energy required for this process is from the fuel to operate the furnace and other forms of energy to operate the auxiliary equipment.

Potential environmental pollutants produced by this process are atmospheric emissions and solid wastes. The atmospheric emissions are composed of dust particles and gases. These are, in most cases, treated in baghouses which collect approximately 99 percent of the particulate matter. The solid waste is generated as slag and, in most cases, is ground at another facility for use in sandblasting or road surfacing operations.

Thus, the smelting process is a potential source of pollution problems. These problems may result from disposal of the baghouse dusts via landfill which could result in contamination of the water system and possibly contamination of the atmosphere with gases and particulate matter from pollution abatement equipment. However, atmospheric emissions do not probably constitute a serious pollution hazard.

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* Conversation with Leonard Arness, ARMCO Steel Advanced Metals Division, P. O. Box 1697, Baltimore, Maryland 21203.

Reactor Finishing (4). This process, very similar to a foundry operation, purifies the metal further and adjusts the composition to the required values.

The process steps are: (a) charging the molten metal to the furnace; (b) adding cold metals such as base scrap and pig nickel; (c) adding lime, silica, and trim (manganese, columbium, titanium, etc., in trace quantities as required by alloy composition); (d) melting the charge; (e) pouring into molds, and (f) removing the slag.

Large amounts of heat energy are required by the process.

Potential pollutants generated by this process are atmospheric emissions containing gases and particulate matter and solid wastes in the form of slag. The atmospheric emissions are treated via a baghouse which removes approximately 99 percent of the particles. The slag is sold as a product for use as a sandblasting material or in road surfacing operations.

Thus, the reactor finishing process has a low potential for the production of serious pollution problems.

Casting Operation

Ingot Casting (5). In this process the molten alloy from the reactor or electric furnace is cast into required shapes.

The process steps are: (a) pouring into molds and (b) removing the ingots from the mold after they are cast by air cooling.

Energy requirements of the process are minimal

Wastes produced are minor amounts of metallic vapor which stays inplant.

The potential pollution of the wastes is insignificant.

Population of Secondary Nickel Processors

(1) Alloy Metal Products, Inc.
626 Schmidt Road
Davenport, Iowa
Telephone: (319) 324-3511

(2) American Nickel Alloy Manufacturing Company
30 Vesey Street
New York, New York 10007

(3) ARMCO Steel Corporation
Advanced Metals Division
P. O. Box 1697
Baltimore, Maryland 21203

(4) Belmont Smelting Company
330 Belmont Avenue
Brooklyn, New York 11207

(5) Frenkel Company
19300 Filer Avenue
Detroit, Michigan
Telephone: 306-5300

(6) Mercer Alloy Corporation
1 Alloy Road
Greenville, Pennsylvania 16123

(7) Metal Bank of America, Inc.
6801 State Road
Philadelphia, Pennsylvania 19135
Telephone: (215) 332-6600

(8) Paragon Smelting Corporation
36-08 Review Avenue
Long Island City, New York 11101
Telephone: (212) 729-3641

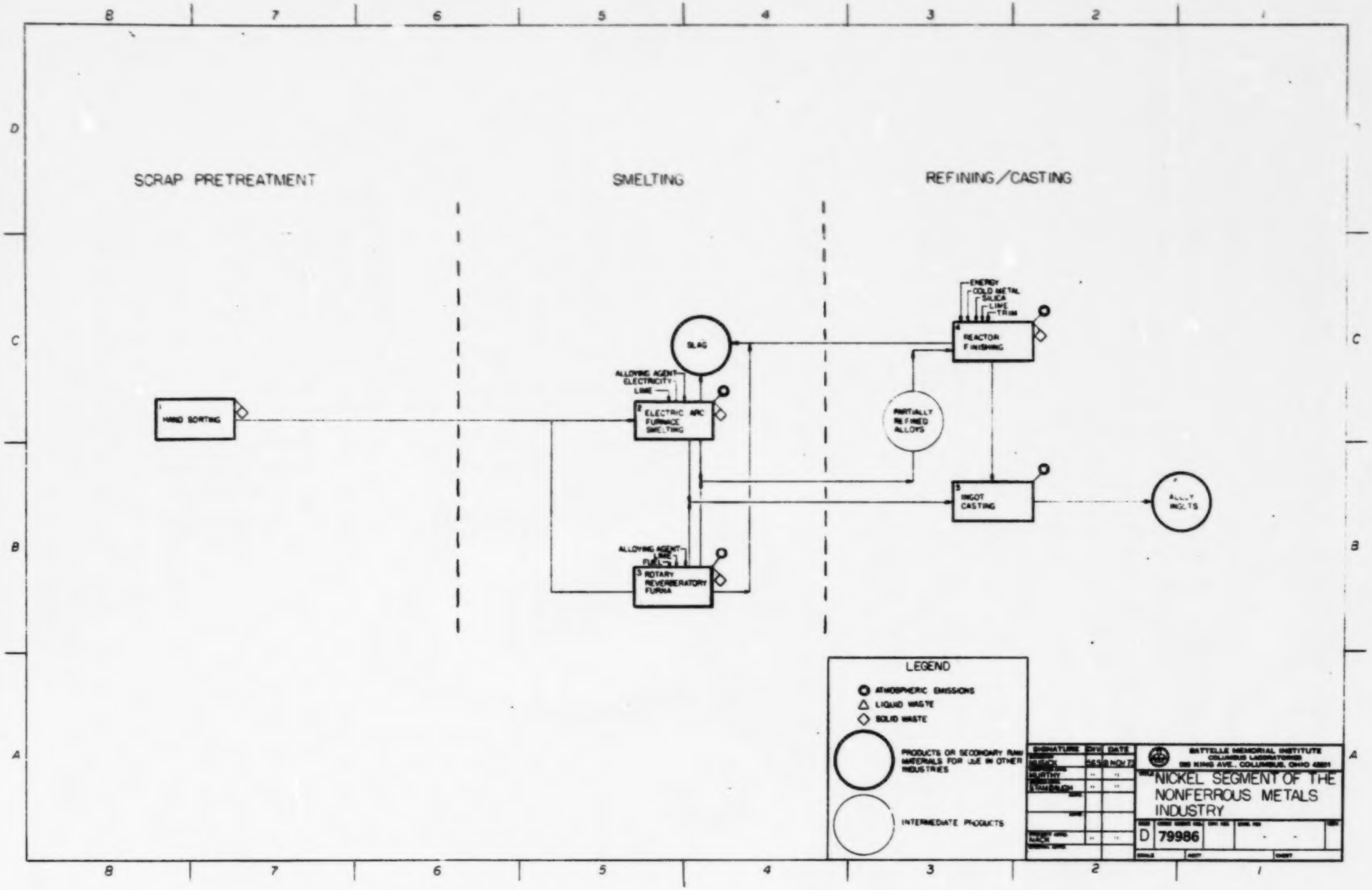
(9) Riverside Alloy Metal
Division of H. K. Porter Company, Inc.
309, Porter Building
Pittsburgh, Pennsylvania 15219
Telephone: (412) 391-1800

(10) I. Schumann Company
Division of Ogden Metals Company
22500 Alexander Road
Cleveland, Ohio

(11) Utica Alloys, Incorporated
Box 53
Utica, New York 13501

(12) Wai Met Alloys Company
7322 Oakman Boulevard
Dearborn, Michigan
Telephone: (313) 581-7200

(13) Whitaker Metals
Alloy Division
P. O. Box 607
Greenville, Pennsylvania 16125


SCRAP PRETREATMENT
SMELTING
REFINING/CASTING
1 HAND SORTING
2 ELECTRIC ARC FURNACE SMELTING
ALLOYING AGENT
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LIME
SLAG
3 ROTARY REVERBERATORY FURNA
ALLOYING AGENT
LIME
FUEL
4 REACTOR FINISHING
ENERGY
COLD METAL
SILICA
LIME
TRIM
PARTIALLY REFINED ALLOYS
5 INGOT CASTING
ALLOY INGOTS
LEGEND
ATMOSPHERIC EMISSIONS
LIQUID WASTE
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NICKEL SEGMENT OF THE NONFERROUS METALS INDUSTRY
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PROCESS DESCRIPTION OF THE PRECIOUS METALS SEGMENT OF THE SECONDARY NONFERROUS METALS INDUSTRY

This segment includes the secondary recovery methods for gold, silver, and platinum group of metals. These are grouped together because they derive from the same scrap and the same general recovery operations are used to obtain the individual metals from the scrap.

Exact statistics on scrap volume are not available. However, estimates are that about 10,000 tons of scrap are processed per year, excluding low grade scrap which is disposed of in landfills at present. These scrap estimates are corroborated by the secondary platinum and silver production figures, the silver consumption of the electronic industry being about 28 percent of the total U. S. silver consumption. Production statistics of this segment from new and old scrap are as follows:

	1971 Production of Precious Metals				
	Secondary		Primary		
	Troy Ounces*	Tons	Troy Ounces	Tons	Percent**
Gold	2.2×10^6	75.5	1.5×10^6	51.2	147%
Silver	47×10^6	1597	69×10^6	2355	68%
Platinum	103,429	3.55	10,198	0.35	1014%

* One troy ounce is equal to 1.1 regular (avdp.) ounce.

** Secondary as a percent of the primary production.

Raw Materials

Electronic components such as gold-plated contacts and printed circuit boards from military and civilian scrap equipment are the chief source of scrap for this segment. The second important source is scrap from the dental industry. Scrap jewelry usually goes to special smelters as these do not require complicated processing. Thus, raw materials to this segment include:

(1) Electronic scrap consisting of relay contacts, switch contacts, wires, solders, etc.
(2) Dental analgams, inlays, dentures, and crowns
(3) New scrap generated in manufacturing.

Products

Products from this segment include:

(1) Refined gold metal

(2) Refined silver metal

(3) Refined platinum metal

(4) Refined palladium and trace quantities of iridium and other metals.

Process Description

The recovery of precious metals from scrap involves three manufacturing operations: (1) scrap pretreatment, (2) smelting, and (3) refining/casting. These operations and the individual processes under each operation are shown in the flowsheet entitled "Precious Metals Segment of The Secondary Nonferrous Metals Industry".

Scrap Pretreatment Operation

Although a variety of processes are possible in scrap pretreatment, only two processes are notably important for detailed consideration.

Hand Sorting and Crushing Process (1). Bulk precious metals scrap consisting of identifiable aluminum contaminants (aluminum chasis) is hand sorted to separate the aluminum from the scrap. The aluminum-free scrap is then crushed in a hammer mill.

The process steps are: (a) spread bulk scrap on floor, (b) pick out aluminum parts, and (c) shred aluminum-free scrap in a hammer mill shredder.

The process requires electrical energy for crushing.

Wastes generated consist of minor in-house dust emissions during charging and discharging of the shredder.

The potential for pollution of wastes in this process is insignificant.

Incineration Process (2). The crushed scrap is incinerated to burn off plastics and organic liquids and prepare a smelter feed.

The processing steps are: (a) charge to incinerator, (b) burn-off combustible constituents, and (c) discharge smelter feed.

The process requires heat energy.

Wastes generated are: (1) atmospheric emissions consisting of organic vapors and dust particles and (2) liquid waste if wet scrubbing is used to control dust particles in the atmospheric emissions.

Untreated wastes have considerable ambient air pollution potential. However, the atmospheric emissions are treated in an afterburner to complete combustion of organic matter. Thus, the effluents from the afterburner contain particles of dust and metal. Usually a wet scrubber or baghouse is used to collect these particles. The amount of dust collected by either of these control devices is not sufficient to constitute serious solid waste problems. Similarly, any liquid waste generated is insignificant.

Therefore, the wastes from this process have no serious pollution potential.

Smelting Operation

Blast Furnace Smelting Process (3). This process purifies the pretreated scrap to produce black copper.

The process steps are: (a) charging the segregated scrap with coke and flux, (b) melting the charge, (c) slagging the melt, (d) discharging black copper, and (e) removing the slag.

Heat energy is the main energy requirement of the process.

Copious amounts of atmospheric emissions and moderate quantities of solid waste--hard slag--are generated in the process. The atmospheric emissions are treated in a baghouse. The collected dust is landfilled. The hard slag is crushed and used in sand blasting operations.

Therefore, the wastes generated in this process do not have significant pollution potential.

Converter Purification (4). The black copper is further purified by oxidizing the contaminating metals with air blown through the heated copper. The end product is bullion (copper rich in precious metals).

The process steps are: (a) charging the converter, (b) blowing the melt, (c) removing the slag, (d) pouring the melt into molds, and (e) casting the ingots.

Heat energy is the main energy requirement.

Wastes generated are: (1) minor amounts of atmospheric emissions and (2) slag metal oxides. The slag metal oxides are recycled to the blast furnace.

Therefore, the process has no significant pollution potential if the atmospheric emissions are controlled.

Refining/Casting Operation

Electrolytic Refining Process (5). The bullion from the converter (as the anode) is electrolytically separated into pure copper (cathode) and precious metal slimes.

The process steps are: (a) charging the electrolyte (copper sulfate - $CuSO_4$), (b) electrolysis, and (c) slime recovery.

Electrical energy is required in this process.

Waste products are limited to minor amounts of gaseous hydrogen and arsine. Quantitatively, these wastes do not represent significant potential for pollution. Arsine is very much below TLV levels.

Chemical Refining Process (6). The precious metals slime from the electrolytic process is refined to isolate each of the precious metals by complex chemical processes.

The process steps are: (a) treating the slime with aqua regia to dissolve the precious metals; (b) precipitate the gold, silver, and platinum with suitable chemical solutions; and (c) melt or ignite to collect gold and silver as grains and platinum and palladium as sponge.

The process requires electrical and thermal energy in moderate quantities.

Wastes include waste liquor discharged to waterways and atmospheric emissions generated during melting and ignition.

The process has a low potential for the production of atmospheric emission problems if emissions are controlled. Discharge of the spent liquor to the waterways could result in pollution problems.

Population of Secondary Precious Metals Industries

(1) Joseph Behr and Sons, Inc.
1100 Seminary Street
Rockford, Illinois
Telephone: (815) 962-7721

(2) Eastern Smelting and Refining Corporation
105 West Brookline Street
Boston, Massachusetts 02118

(3) Handy and Harman
850 Third Avenue
New York, New York 10022
Telephone: (212) 752-3400

(Refining of precious metal scrap is carried out in
Fairfield, Connecticut and Los Angeles, California)

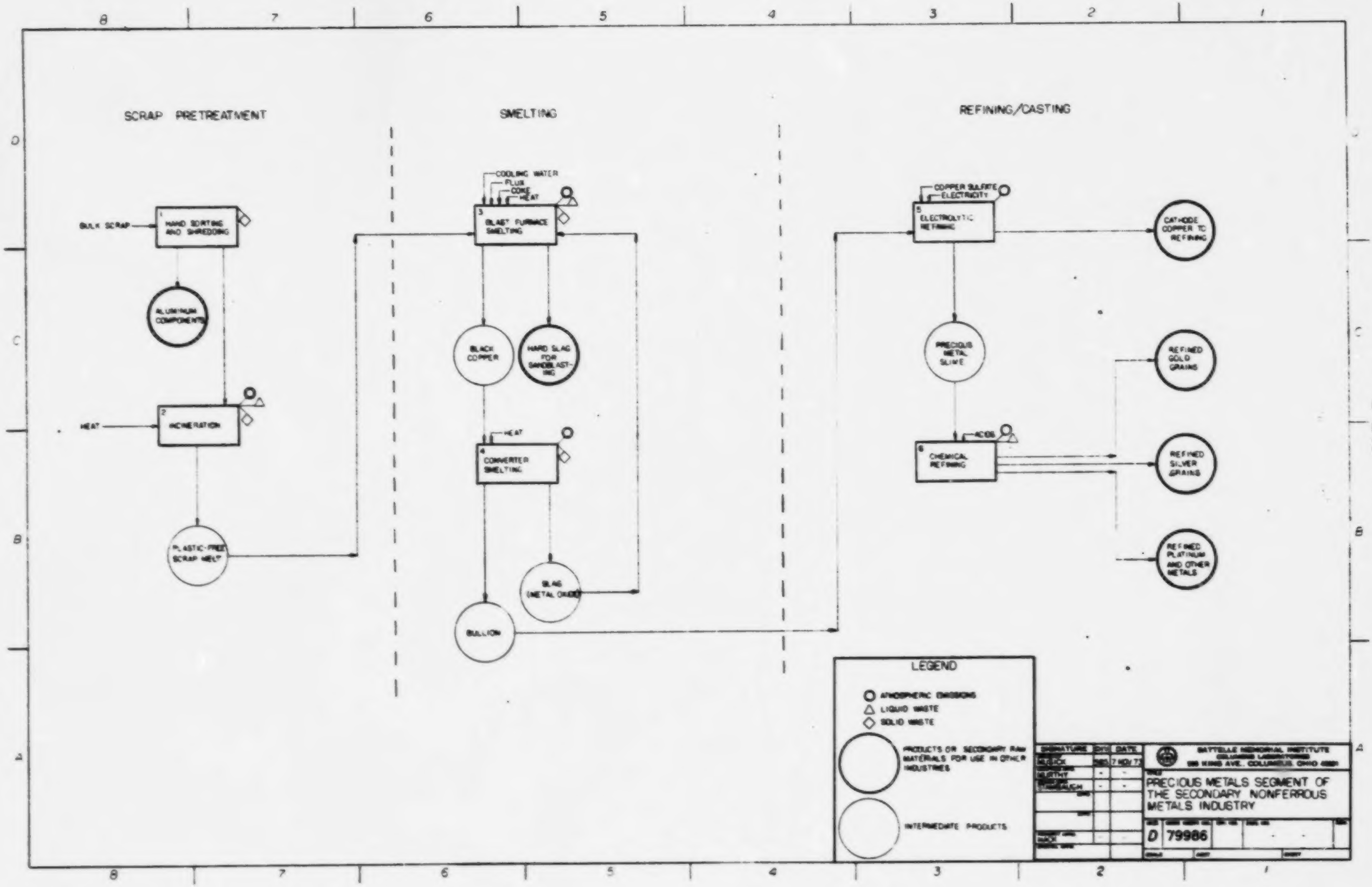
(4) Hudsar, Inc.
567 Wilson Avenue
Newark, New Jersey 07105
Telephone: (201) 642-7334

(5) Metallurgical Products Company
35th and Moone Streets
Philadelphia, Pennsylvania 48300
Telephone: (215) 394-8300

(6) Pease and Curren, Inc.
780 Allens Avenue
Providence, Rhode Island 02905
Telephone: (401) 461-6340

(7) Phelps Dodge Refining Corporation
300 Park Avenue
New York, New York
Telephone: (212) 751-3200

(8) United States Metals Refining Company
1270 Avenue of the Americas
New York, New York 10020
Telephone: (212) 757-9700


SCRAP PRETREATMENT
SMELTING
REFINING/CASTING
BULK SCRAP
1 HAND SORTING AND SHREDDING
ALUMINUM COMPONENTS
HEAT
2 INCINERATION
PLASTIC-FREE SCRAP METAL
COOLING WATER
FLUX
COKE
HEAT
3 BLAST FURNACE SMELTING
BLACK COPPER
HARD SLAG FOR SANDBLASTING
HEAT
4 CONVERTER SMELTING
SLAG (METAL OXIDE)
BULLION
COPPER SULFATE
ELECTRICITY
5 ELECTROLYTIC REFINING
CATHODE COPPER TO REFINING
PRECIOUS METAL SLIME
ACIDS
6 CHEMICAL REFINING
REFINED GOLD GRAINS
REFINED SILVER GRAINS
REFINED PLATINUM AND OTHER METALS
LEGEND
ATMOSPHERIC EMISSIONS
LIQUID WASTE
SOLID WASTE
PRODUCTS OR SECONDARY RAW MATERIALS FOR USE IN OTHER INDUSTRIES
INTERMEDIATE PRODUCTS
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BATTELLE MEMORIAL INSTITUTE
COLUMBUS LABORATORIES
505 KING AVE., COLUMBUS, OHIO 43201
PRECIOUS METALS SEGMENT OF THE SECONDARY NONFERROUS METALS INDUSTRY
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PROCESS DESCRIPTION OF SELENIUM SEGMENT OF SECONDARY NONFERROUS METALS INDUSTRY

Tonnage-wise, the selenium segment constitutes one of the minor segments of the secondary nonferrous metals industry. Based on 1971 data, 30,000 lbs or about 3 percent of the total U. S. consumption was recovered from scrap. Wastes from this segment are atmospheric emissions, liquid wastes, and solid wastes.

Raw Materials

Sources of raw materials for this segment, including both new and old scrap, are:

(1) Selenium rectifiers (burned out and factory rejects)
(2) Spent catalysts
(3) Used xerographic plates.

Products

The product from this segment is metallic selenium in the form of shot, refined powder, and selenium ingots.

Process Description

The recovery of selenium from selenium scrap involves three manufacturing operations: scrap pretreatment, smelting/refining, and casting (product formation). These operations and the individual processes under each operation are shown on the flowsheet entitled "Selenium Segment of the Secondary Nonferrous Metals Industry".

Scrap Pretreatment

Selenium is separated from the majority of the other scrap components in the scrap pretreatment operation.

Mechanical Process (1). The selenium is separated from the other scrap components by hammer-milling, shot blasting, and similar methods. The recovered selenium is further processed or sold as a selenium metal.

Energy demand is that needed to drive the equipment.

The process produces atmospheric emissions and solid wastes. The atmospheric emissions contain particulates of selenium metal, compounds, alloys, and oxide, whereas the solid wastes are composed of metallic and nonmetallic scrap.

Smelting/Refining Operation

In the smelting/refining operation, the pretreated scrap is purified to produce selenium metal for subsequent processing. The processes by which the purification is achieved are Numbers 2 through 4 on the flowsheet.

Retort Smelting Process (2). In retort smelting, partial purification of the pretreated scrap is achieved and the scrap is densified. The process steps are: (1) charging the retort, (2) melting the scrap, (3) separating the selenium from the impurities by distillation, and (4) discharging the residue from retort.

The energy required is that needed to heat the retort.

Potential environmental pollutants are atmospheric emissions, solid wastes, and liquid wastes. The atmospheric emissions are composed of gases and particulate matter containing selenium. The solid wastes contain the impurities from the scrap selenium. These wastes may go to landfill. The liquid waste is cooling water which may be recycled in most cases.

Thus, retort smelting has the potential for producing atmospheric pollution problems as well as water pollution problems from leaching in the landfill.

Hydrometallurgical Refining (3). Hydrometallurgical refining also achieves a partial purification of the scrap selenium. The process steps are: (1) dissolve the scrap selenium or the selenium from Process 2 in a suitable solvent such as aqueous sodium sulfite, (2) remove insoluble impurities by filtration, and (3) precipitate the selenium for further purification.

The energy required is that needed to heat the solutions and operate the auxilliary equipment.

Potential environmental pollutants are atmospheric emissions if gases are used to precipitate the selenium, liquid wastes, and solid wastes. The process has the potential for the generation of pollution problems.

Distillation Process (4). This process yields high-purity selenium. The process steps are: (1) charge the distillation unit, (2) melt and distill the selenium, (3) condense the selenium vapors, (4) transfer molten selenium to the product formation operation, and (5) remove residue from the still.

The energy required is that needed to operate the distillation unit.

Potential pollutants are atmospheric emissions composed of distillation wastes and particulates of selenium, solid wastes, and liquid wastes. This process also has the potential for the production of pollution problems.

Product Formation Operation

In product formation, the molten selenium is converted to the desired shape. The processes used to achieve this are Processes 5 and 6.

Quenching Process (5). The quenching process produces selenium shot and selenium powder. The process steps for the production of selenium shot are: (1) quench the selenium melt in a quenching liquid, (2) separate the shot from the cooling liquid, and (3) dry the shot. Powder is produced by quenching the selenium vapors from the distillation unit.

Energy required is that needed to cool the quenching medium and operate the auxilliary equipment.

Potential pollutants are liquid wastes such as cooling water which is recycled in most cases. The process has a low potential for the production of pollution problems.

Casting Process (6). By this process, the molten selenium is cast into ingots or other shapes. The process steps are: (1) pour the molten selenium into the molds and (2) solidify the melt.

Energy is needed to operate the equipment.

Essentially no pollutants are emitted. Thus, the process has no potential for the production of pollution problems.

Population of Secondary Selenium Processors

(1) Kawecki-Berylco Industries
Box 1462
Tuckertown Road
Reading, Pennsylvania 19603

(2) American Smelting and Refining Company
3422 South 700 West
Salt Lake City, Utah 84119

(3) U. S. Metals Refining Company
Division of American Metals Climax, Inc.
300 Middlesex Avenue
Carteret, New Jersey

(4) Eastern Metal Converters, Inc.
52 Wall Street
New York, New York
Telephone: 4-5778

(5) Kawecki-Berylco Industries, Inc.
220 E. 42nd Street
New York, New York

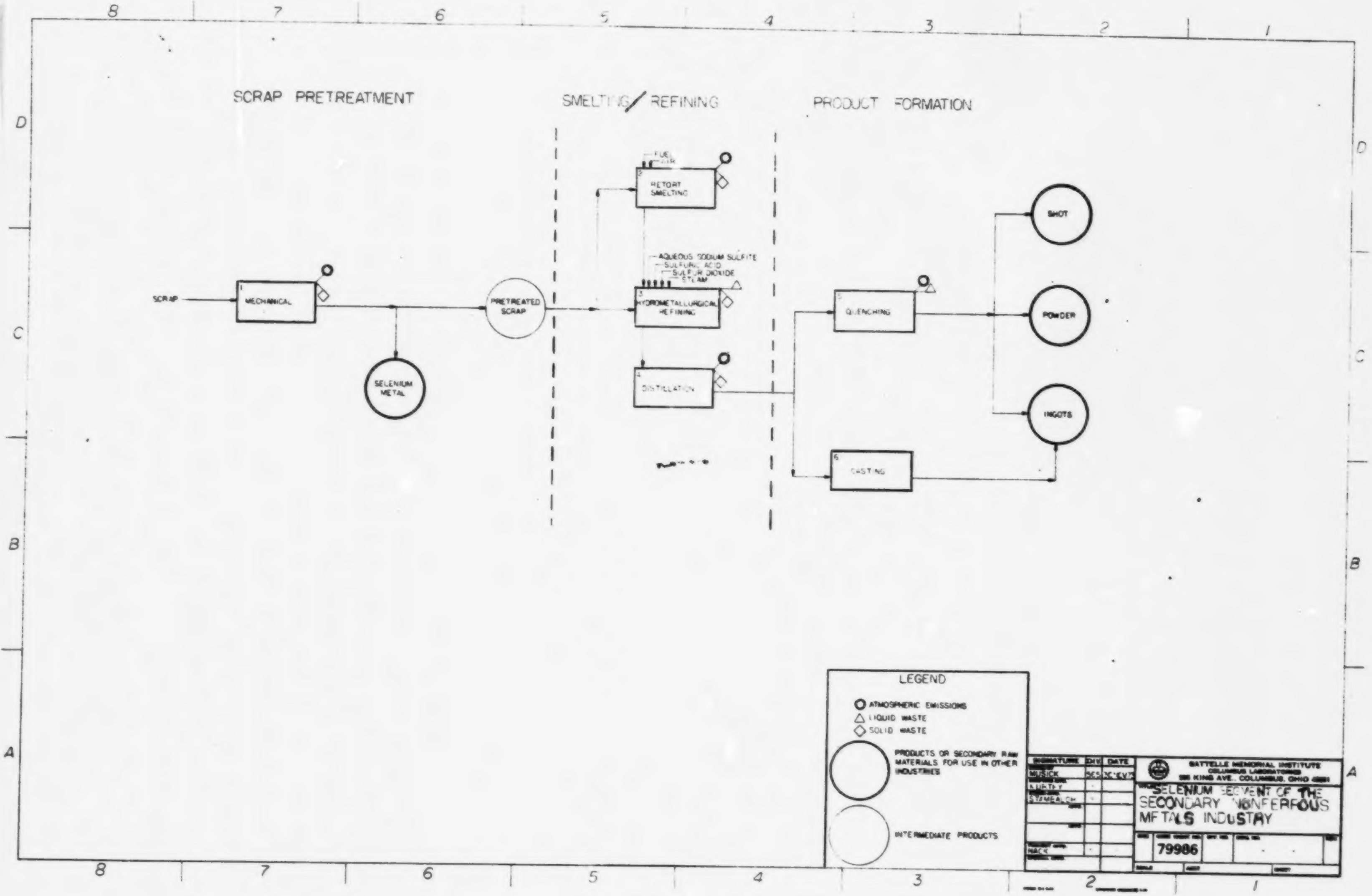
(6) Metallurgical Products Company
35th and Moore Streets
Philadelphia, Pennsylvania
Telephone: 344-8300

(7) Max Zuckerman and Sons
Music Fair Road
Owings Mills, Maryland 21117
Telephone: (301) 484-0400

(8) Phelps Dodge Refining Corporation
300 Park Avenue
New York, New York

(9) Belmont Smelting and Refining Works
320 Belmont Avenue
Brooklyn, New York 11207
Telephone: (212) 624-4004

(10) Alloy Chem, Inc.
641 Lexington Avenue
New York, New York 10022
Telephone: (212) 421-6300


SCRAP PRETREATMENT
SMELTING/REFINING
PRODUCT FORMATION
SCRAP
1 MECHANICAL
SELENIUM METAL
PRETREATED SCRAP
FUEL
AIR
2 RETORT SMELTING
AQUEOUS SODIUM SULFITE
SULFURIC ACID
SULFUR DIOXIDE
STEAM
3 HYDROMETALLURGICAL REFINING
4 DISTILLATION
QUENCHING
6 CASTING
SHOT
POWDER
INGOTS
LEGEND
ATMOSPHERIC EMISSIONS
LIQUID WASTE
SOLID WASTE
PRODUCTS OR SECONDARY RAW MATERIALS FOR USE IN OTHER INDUSTRIES
INTERMEDIATE PRODUCTS
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COLUMBUS LABORATORIES
505 KING AVE., COLUMBUS, OHIO 43201
SELENIUM SEGMENT OF THE SECONDARY NONFERROUS METALS INDUSTRY
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PROCESS DESCRIPTION OF THE TIN SEGMENT OF THE SECONDARY NONFERROUS METALS INDUSTRY

The importance of the tin segment of the secondary nonferrous metals industry is highlighted by the fact that virtually all U. S. primary tin requirements (69,029 tons in 1972) are imported and that the secondary production constitutes about one-third of total U. S. production. In 1972, this amounted to 20,180 long tons. The forecast demand for tin for the year 2000 is about 120,000 long tons.

Additional salient tin recovery statistics for the U. S.(1) are provided below.

	1967	1971	1972
Secondary tin recovered (long tons)	21,000	20,096	20,180
U. S. tin consumption (long tons)	82,000	69,950	69,029
Percent secondary tin recovery	25.6	28.7	29.2
Percent as primary tin	16	10	10
Percent as alloy, etc.			

Minor sources of air pollution are the dross smelting and gas fired refining processes. The water pollution potential from the chemical detinning operation is the major pollution problem of the tin scrap recovery segment.

Raw Materials

Major raw material sources for scrap recovery are the trimmings and rejects from the can companies and rejected plating coils from the steel industry. Although the used food cans and containers constitute a vast potential source of raw material, their present contribution to the recoverable scrap is only one percent. Even this one percent is collected by the ecology minded groups like the Isaac Walton group, etc. Other than these groups, there is no organized method of used can collection for scrap recovery. Almost 99 percent of the used cans find their way to municipal incinerators.

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(1) U. S. Bureau of Mines, Washington, D. C., Telephone Conversation with Keith Harris.

The recovery of scrap from used cans is not expected to exceed the current level because of the aluminum and plastic used in production of cans. The high cost of segregating the tin and iron metal portion from the garbage and the difficulties in processing the metal cans to recover the tin in the presence of aluminum are negative incentives to increased usage of used cans in scrap recovery. Thus, the raw materials are mostly new scrap consisting of:

(1) Tin drosses and sludges
(2) Solder drosses and sludges
(3) Can rejects from can companies
(4) Rejected plating cells
(5) Bronze used parts and rejects
(6) Type metal scrap.

Products

Products from the tin segment of the secondary nonferrous metals industry include:

(1) Pig tin
(2) Solder and type metal (tin-lead alloy with varying amounts of antimony)
(3) Tin oxide
(4) Fire-refined tin
(5) Sodium stannate
(6) Stannous sulfate and other tin chemicals
(7) Babbit metal.

Process Description

Three manufacturing operations are employed to recover tin from scrap: (1) scrap pretreatment, (2) detinning/smelting, and (3) refining/casting. These operations and the associated processes are shown in the process flowsheet for the tin segment of the secondary nonferrous metals industry.

Scrap Pretreatment Operation

The pretreatment process varies according to the type of scrap. The individual pretreatment processes are Numbers 1 and 2 on the segment flowsheet.

Dealuminization Process (1). This process is conducted only if the scrap tin cans are suspected to contain substantial quantities of aluminum ends. About 90 percent of the time dealuminization is not done.

This process removes aluminum as sodium aluminate in solution. The steps are: (a) leach the scrap in hot sodium hydroxide, (b) remove the sodium aluminate solution, (d) pump it to Process No. (7) of the refining operation for recovery of soluble tin values, and (d) recover dealuminized tin scrap for Process No. (3).

Heat energy for alkali solution and electrical energy for pumping are required.

The process produces no wastes; hence, there is no potential pollution from this process.

Batch Mixing Process (2). This mechanical operation mixes the drosses with limestone and coke to prepare a feed suitable for smelting.

Mixing is the only process step involved.

Electrical energy for the rotary drum mixer is required.

Dust emissions are produced. However, these are collected by baghouses and recycled. The process, therefore, has no pollution potential.

Detinning-Smelting Operation

By the detinning-smelting operation, the tin values in scrap are separated from metallic and nonmetallic impurities or contaminants. Two types of operation--hydrometallurgical and pyrometallurgical--are used. The individual processes are numbered 3 through 5 in the flowsheet.

Chemical Detinning Process (3). The process extracts the tin value in the scrap as sodium stannate solution and also generates detinned steel scrap for use in secondary ferrous metallurgy.

The process steps are: (a) addition of hot alkali (NaOH) and sodium nitrite or nitrate ($NaNO_2$ or $NaNO_3$) solution to the scrap, (b) draining and pumping the solution to the refining/casting operation after the reaction is complete, and (c) washing the detinned scrap with water sprays (as many as four) to obtain clean scrap for the steel industry. Three of the sprays are pumped to the crude sodium stannate solution tank and the fourth spray is used for recycle.

Heat energy is required to heat the caustic solution and electrical energy for pumping stannate solution and spray water.

No significant quantities of wastes are generated in the process and hence there are no serious pollution problems.

Dross Smelting Process (4). This process partially purifies the drosses and produces "crude furnace metal".

The process steps are: (a) charging the furnace, (b) melting the charge, (c) tapping the "crude furnace metal", and (d) tapping matte and slag.

Heat energy is required in smelting. It is reported(2) that 90 gallons of fuel oil per ton of charge are used in the process.

The matte produced is shipped to the copper smelter. The slag is discarded if low in metal values. Cooling water is recycled in a closed loop operation. Hence, the only wastes are minor atmospheric wastes and major amounts of slag. Almost 99.9 percent of dust in the furnace gases is collected in an electrical precipitator and leached in Process (5).

The process has reasonable potential for solid waste pollution.

Dust Leaching and Filtration Process (5). The tin and chlorine values in the Cottrel dust collected in Process (4) are separated from the dust by sulfuric acid leaching. The process steps are: (a) leaching the Cottrel dust with dilute sulfuric acid to remove zinc and chlorine, (b) filtering to remove acid and dissolved zinc and chlorine, (c) drying the leached dust, and (d) conveying the dried leached dust to Process (2).

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(2) Earl R. Marble, Jr., "Redesigning a Secondary Smelting Plant", Journal of Metals, pp 218-222, March, 1951.

Energy required for this process is electrical energy and that derived from fuel oil.

Potential environmental pollutants generated by this process are atmospheric emissions from handling of the dust and drying of the leached dust, liquid wastes from the leaching and filtering steps, and solid wastes collected via a baghouse from the atmospheric emissions.

Thus, the process has a potential for the production of pollution problems if the pollutants are not collected and disposed of in an acceptable manner.

Refining/Casting Operation

Via this operation, the tin is recovered as sodium stannate of commerce, as stannic oxide, as pure metallic tin, and as tin alloys. The individual processes to produce these products are 6 through 13 as noted in the flowsheet.

Settling and Leaf Filtration Process (6). This process produces a purified stannate solution from which tin can be recovered by a number of processes. The impurities--silver, mercury, copper, cadmium, some iron, cobalt, and nickel--are precipitated as metal sulfides.

The process steps are: (a) addition of sodium sulfide with agitation, (b) settling, (c) decantation, and (d) filtration.

Electrical energy is required for agitation and filtration steps.

The process has marginal potential for solid waste disposal problems. These solid wastes are generated as metal sulfides.

Evapocentrifugation (7). This process produces a sodium stannate of commerce (Na_2SnO_3) product.

The process steps are: (a) heating the solution to concentrate the sodium stannate solution, (b) crystallization of sodium stannate, and (c) recovery of the stannate by centrifugation.

Thermal energy for evaporation and electrical energy for centrifugation are required.

The wastes produced are atmospheric emissions consisting of water vapor and liquid wastes.

The process has no substantial pollution potential.

Electrolytic Refining Process (8). This process produces cathodic pure tin metal from the purified sodium stannate solution. The process steps are: (a) passing the alkaline electrolyte (sodium stannate solution) through a cascade of cells at about 190 F, a characteristic condition with an initial concentration of 110-120 g/l of tin; (b) removal of cathode as tin builds up; and (c) stripping the tin from the cathode.

Electrical energy is required for electrolysis and to operate auxiliary equipment.

Spent electrolyte, an alkaline solution, is generated as a liquid waste. This waste has moderate water pollution potential.

Acidification and Filtration Process (9). The process produces "tin hydrate" which is subsequently processed to tin and stannic oxide.

The process steps are: (a) acid neutralization with sulfuric acid to form "tin hydrate" and (b) filtration to separate the hydrate as filter cake. The filtrate is recycled to Process (6).

Electrical energy is used for stirring and filtration.

No wastes per se are generated in the process and hence the process has no pollution potential.

Fire-Refining (10). This process produces purified tin from cathodic tin. Natural gas is the heat source. The process steps are: (a) charging the furnace, (b) melting of the charge, (c) removing the impurities as slag and dross, (d) pouring of the molten metal, and (e) casting of the metallic tin.

Energy required for this process is that derived from natural gas.

Potential pollutants are atmospheric emissions--gases and metallic fume--and solid wastes. The solid wastes are recycled for metals recovery. Thus, the process is not a source of serious pollution problems.

Smelting Process (11). This is an alternate route to producing pure tin when electrolysis is not feasible. The process converts the tin hydrate to tin metal by reducing the stannic oxide (SnO_2) with a reducing agent.

The process steps are: (a) heating the hydrate, (b) adding the reducing agent, (c) reducing the tin hydrate, (d) melting the tin, (e) skimming the dross, (f) pouring the molten metal, and (g) casting the metal.

Heat energy derived from the fuel is the main energy requirement of the process.

Potential pollutants are solid wastes, liquid wastes, and atmospheric emissions. The solid waste produced as dross is recycled. The water used to cool castings is recycled although eventually some of it is rejected to the waterways. Atmospheric emissions are collected via baghouses or wet scrubbers.

The pollution potential of the process does not appear to be significant.

Calcining Process (12). This process converts tin hydrate to anhydrous stannic oxide (SnO_2). The process steps consist of: (a) charging the calciner, (b) calcining the tin hydrate, and (c) removing and packaging the stannic oxide.

Energy required is thermal energy.

The primary pollutant is atmospheric emissions consisting of water vapor, dusts, and fume. Solid wastes generated are those collected in the baghouse.

Thus, this process has a potential for the production of pollution problems.

Kettle Refining Process (13). This process purifies the "crude furnace metal". The process steps are: (a) dry drossing to remove the impurities as slag and matte, (b) decopperizing using sulfur, (c) removing antimony using aluminum, and (d) casting into required shapes.

The process uses large amounts of heat energy as derived from fuel oil.

The waste products generated are atmospheric emissions and solid wastes. The solid wastes are slag and matte from the purification of the crude furnace metal. Atmospheric emissions consist of gases from combustion of the fuel and fume and dust entrained in the gases.

These wastes constitute reasonable potential for pollution if not collected and disposed of by an approved method.

Population of Secondary Tin Processors

(1) Colonial Metals Company
Columbia, Pennsylvania
Telephone: (717) 684-2311

(2) K. Hettlemen & Sons
Division of Minerals & Chemicals
Phillip Corporation
9th Street & Patapsco Avenue
Baltimore, Maryland 21225
Telephone: (301) 355-0770

(3) Holtzman Metal Company
5223 McKissock Street
St. Louis, Missouri 63147
Telephone: (314) 244-3820

(4) Industrial Smelting Company
19430 Mt. Elliot at Marx Street
Detroit, Michigan
Telephone: (313) 892-5300

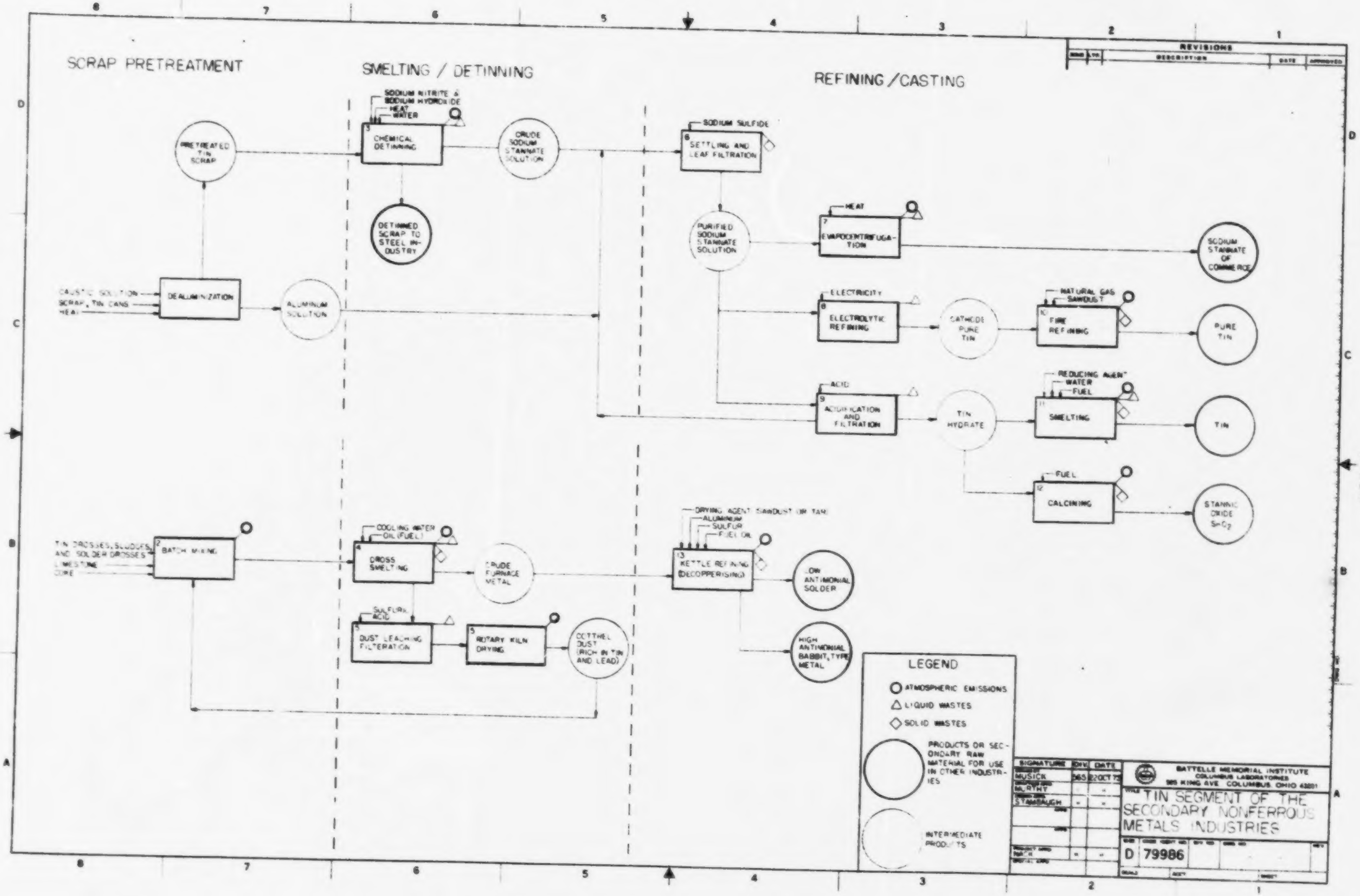
(5) Inland Metals & Refining Company
651 East 119th Street
Chicago, Illinois 60628
Telephone: (312) 928-6767

(6) M & T Chemicals
Rahway, New Jersey

(7) North American Smelting Company
Marine Terminal P. O. Box 1952
Wilmington, Delaware
Telephone (302) 654-9901

(8) United States Metal Products Company
P. O. Box 1067
Erie, Pennsylvania 16512
Telephone: 838-2051

(9) Vulcan Materials Company
Metallics Division
Edison, New Jersey
Telephone: (201) 225-3838


SCRAP PRETREATMENT
SMELTING / DETINNING
REFINING / CASTING
CAUSTIC SOLUTION
SCRAP, TIN CANS
HEAT
DEALUMINIZATION
PRETREATED TIN SCRAP
ALUMINUM SOLUTION
SODIUM NITRITE & SODIUM HYDROXIDE
HEAT
WATER
3 CHEMICAL DETINNING
DETINNED SCRAP TO STEEL INDUSTRY
CRUDE SODIUM STANNATE SOLUTION
SODIUM SULFIDE
6 SETTLING AND LEAF FILTRATION
PURIFIED SODIUM STANNATE SOLUTION
HEAT
7 EVAPOCENTRIFUGATION
SODIUM STANNATE OF COMMERCE
ELECTRICITY
8 ELECTROLYTIC REFINING
CATHODE PURE TIN
NATURAL GAS
SAWDUST
10 FIRE REFINING
PURE TIN
ACID
9 ACIDIFICATION AND FILTRATION
TIN HYDRATE
REDUCING AGENT
WATER
FUEL
11 SMELTING
TIN
FUEL
12 CALCINING
STANNIC OXIDE SnO_2
TIN DROSSES, SLUDGES, AND SOLDER DROSSES
LIMESTONE
COKE
2 BATCH MIXING
COOLING WATER
OIL (FUEL)
4 DROSS SMELTING
CRUDE FURNACE METAL
SULFURIC ACID
5 DUST LEACHING FILTERATION
5 ROTARY KILN DRYING
COTTREL DUST (RICH IN TIN AND LEAD)
DRYING AGENT SAWDUST OR TAR
ALUMINUM
SULFUR
FUEL OIL
13 KETTLE REFINING (DECOPPERISING)
LOW ANTIMONIAL SOLDER
HIGH ANTIMONIAL BABBIT, TYPE METAL
LEGEND
○ ATMOSPHERIC EMISSIONS
△ LIQUID WASTES
◇ SOLID WASTES
PRODUCTS OR SECONDARY RAW MATERIAL FOR USE IN OTHER INDUSTRIES
INTERMEDIATE PRODUCTS
REVISIONS
DESCRIPTION
DATE
APPROVED
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MUSICK
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MURTHY
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BATTELLE MEMORIAL INSTITUTE
COLUMBUS LABORATORIES
505 KING AVE COLUMBUS, OHIO 43201
TIN SEGMENT OF THE SECONDARY NONFERROUS METALS INDUSTRIES
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PROCESS DESCRIPTION OF THE TITANIUM SEGMENT OF THE SECONDARY NONFERROUS METALS INDUSTRY

The titanium segment of the secondary nonferrous metals industry constitutes one of the minor segments. Annual recovery of titanium is approximately 8000 tons. Because of the nature of the operations, this segment has a low potential for the production of serious atmospheric emission problems. However, problems resulting from water pollution could be significant.

Raw Materials

Raw materials to this segment include the following:

(a) Bulk scrap (trim sheets, plate sheets, cuttings, etc.)
(b) Noncarbide machine turnings and borings
(c) Carbide-containing machine turnings and borings. This scrap is generated by the use of carbide tools in machining.

Products

Products include titanium alloy ingots and electrodes.

Population of Companies

The following companies are known to be involved in titanium scrap processing:

(1) RMI Company
Niles, Ohio
Telephone (216) 652-9951

(2) Titanium Metals Corporation of America
West Caldwell, New Jersey

The Air Force Materials Laboratory (AFML) of The Wright-Patterson AFB is also pursuing recovery of the titanium values in scrap. Mr. Lee Kannard (Telephone 513-255-2413) is working to recovery (by contracts to processors) titanium from low-grade scrap generated during machining of parts for aircraft.

Process Description

The recovery of titanium alloys from scrap titanium involves three operations: (1) scrap pretreatment, (2) smelting, and (3) casting. These are shown in the flowsheet entitled "Titanium Segment of the Secondary Nonferrous Metals Industry".

Scrap Pretreatment Operation

Two processes are used in this operation: vapor degreasing and acid pickling. Normally, if the scrap is not contaminated by oxides, acid pickling is not necessary and degreasing will suffice to produce a clean scrap.

Vapor Degreasing (1). This process removes grease and cutting oils from machine turnings and borings.

The process steps are: (1) vaporizing a solvent such as trichloroethylene, (2) mixing the vapors with the scrap, (3) condensing the oil-bearing vapor, (4) filtering the condensed solvent, and (5) removing the scrap for subsequent processing. As the solvent goes through this cycle, the oil dissolves in the solvent and gradually lowers the boiling point of the solvent mixture. Eventually, the oil-solvent mixture is discarded due to loss of deoiling ability of the solvent or the solvent is regenerated.

Heat energy is required by the process for vaporizing the oil and electrical energy for water circulation through condenser.

Wastes generated are the oil-solvent mixture, minor amounts of solvent vapor and insignificant quantities of solid dust particles.

The oil-solvent mixture has a considerable water pollution potential. Atmospheric emissions and solid wastes generated are negligible and thus, present no serious pollution problems.

Acid Pickling Process (2). This process is done only when the scrap is known to contain oxide-scale formed during machining and storage. The process follows vapor degreasing and consists of treating the scrap with a mixture of hydrochloric and hydrofluoric acids. The process steps are: (1) leach the scrap with the mixed acid to remove the oxide, (2) remove the acid from the scrap with a water wash, and (3) dry the scrap for further processing.

Energy requirements are not significant. The major waste generated is a liquid waste consisting of the spent acid mixture. This spent acid is normally disposed of by neutralization.

The process has little potential for the production of serious atmospheric problems. However, the potential for water pollution by spent acids could be significant.

Refining Operation

The scrap pretreatment operation removes primarily the surface impurities such as the oils and the oxide. Via the smelting refining operation the scrap is densified and the internal impurities are removed by vaporization as shown in the segment flowsheet by Process 3.

Vacuum Electric Arc Melting Process (3). In this process, the clean scrap is melted to obtain molten alloys and the volatile impurities are removed. The process steps are: (1) charging clean scrap to the electric furnace, (2) melting the scrap, (3) vaporizing the impurities, and (4) pouring the molten metal.

Energy required is electricity to operate the process.

The process is conducted in a completely closed system and wastes generated are well controlled. Therefore, the process has little potential for the production of pollution problems.

Casting Operation

Casting Process. By this process the molten metal is cast into ingots.

The process consists of: (1) pouring the molten alloy into molds and (2) casting.

Energy requirement is that necessary to operate the equipment.

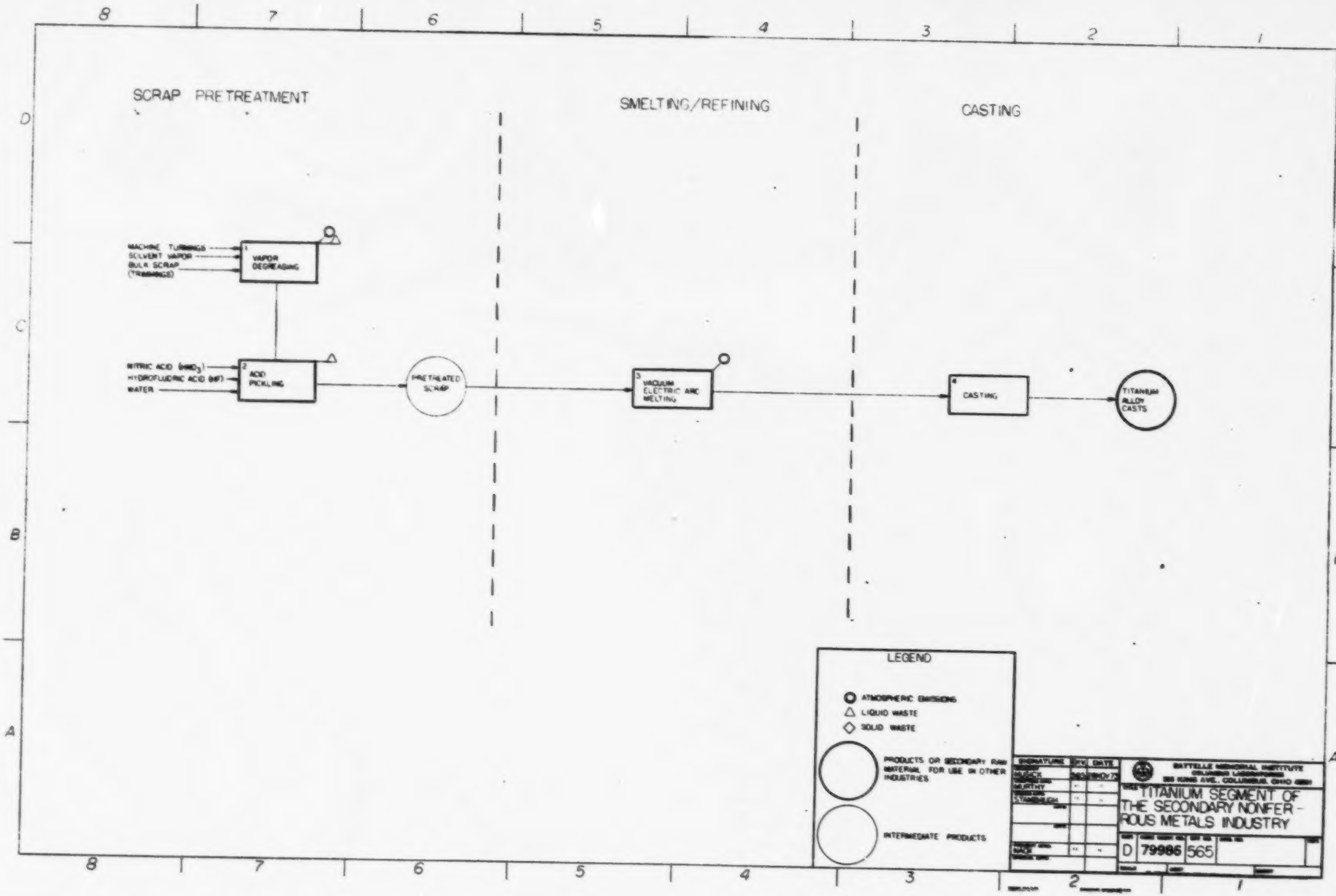
Wastes generated are insignificant and do not present any pollution problem.

Population of Secondary Titanium Processors

(1) RMI Company
Niles, Ohio
Telephone: (216) 652-9951

(2) Titanium Metals Corporation of American
1140 Bloomfield Avenue
West Caldwell, New Jersey
Telephone: (201) 575-9400

(3) Kawecki Berylco Industries, Inc.
220 East 42nd Street
New York, New York


SCRAP PRETREATMENT
SMELTING/REFINING
CASTING
MACHINE TURNINGS
SOLVENT VAPOR
BULK SCRAP (TRIMMINGS)
1 VAPOR DEGREASING
NITRIC ACID (HNO_3)
HYDROFLUORIC ACID (HF)
WATER
2 ACID PICKLING
PRETREATED SCRAP
3 VACUUM ELECTRIC ARC MELTING
4 CASTING
TITANIUM ALLOY CASTS
LEGEND
○ ATMOSPHERIC EMISSIONS
△ LIQUID WASTE
◇ SOLID WASTE
PRODUCTS OR SECONDARY RAW MATERIAL FOR USE IN OTHER INDUSTRIES
INTERMEDIATE PRODUCTS
SIGNATURE
DATE
MURTHY
STAMBAUGH
BATTELLE MEMORIAL INSTITUTE
COLUMBUS LABORATORIES
505 KING AVE., COLUMBUS, OHIO
TITANIUM SEGMENT OF THE SECONDARY NONFERROUS METALS INDUSTRY
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PROCESS DESCRIPTION OF ZINC SEGMENT OF THE SECONDARY NONFERROUS METALS INDUSTRY

Introduction

The zinc segment of the secondary nonferrous metals industry consists of those plants that process discarded and scrap materials for the purpose of recovering zinc. In 1969,(1) 376,400 tons of zinc were recovered. In the recovery of the zinc, waste products--atmospheric emissions, liquid wastes, and solid wastes--are generated which can cause serious pollution problems.

Raw Materials

The principal sources of zinc scrap as classified by the Bureau of Mines(1) are:

New clippings
Old zinc
Engravers' plates
Skimmings and ashes
Sal skimmings
Die-cast skimmings
Galvanizers' dross
Diecastings
Rod and die scrap
Flue dust
Chemical residues.

In addition to containing metallic zinc or compounds and alloys, thereof, the scrap contains a wide variety of organic materials such as oil, grease, lubricants, and electric insulation. Alloying elements commonly found in the scrap are aluminum, copper, and lead.

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(1) Moulds, D. E., Minerals Yearbook, 1969, U. S. Dept. of Interior, Bureau of Mines, p 1148 (1971).

Products

Products from the zinc segment of the secondary nonferrous metals industry are: (1) specification zinc alloys, (2) zinc ingots (slab) containing essentially 100 percent zinc, (3) zinc dust, (4) zinc oxide approaching 100 percent purity, and (5) crude zinc oxide for reduction to zinc metal by the primary smelters.

Process Description

The products from the zinc segment are recovered from the various types of scrap zinc employing two manufacturing operations--scrap pretreatment and refining. These operations and the individual processes in each operation are shown in the attached segment flowsheet.

Scrap Pretreatment Operation

Zinc scrap is pretreated prior to refining to remove a portion of the metallic and nonmetallic impurities and to physically prepare the material for further processing. Three types of preprocessing (hydrometallurgical, pyrometallurgical, and mechanical) are used. The pretreatment varies depending on the type of scrap. The individual pretreatment processes are numbers 1 through 6, as shown in the segment flowsheet.

Crushing/Screening Process (1). The concentration of metallic zinc in skimmings/residues is increased by the crushing/screening process. The process steps involved are: (a) pulverizing or crushing the skimmings/residues to separate the metallic zinc from the flux, and (b) screening or pneumatically treating the crushed material to separate zinc from nonmetallic constituents.

Energy required is that to drive the equipment.

The process generates atmospheric emissions and solid wastes. The atmospheric emissions are composed of dusts from both the pulverizing (crushing) process step and the screening step. These emissions contain, in addition to zinc, those materials--nonmetallic constituents, metallic values such as zinc, aluminum, copper, iron, lead, cadmium, tin, and chromium and fluxes--separated from the scrap zinc during the sweating process. Emissions data are not available; however, based on studies conducted of other industries, the raw emissions factor is estimated to range from 0.9 to 7.5 lb per ton of skimmings/residues processed.

The solid wastes generated by this process are nonmetallic constituents from the screening operation and baghouse dusts, if emissions from crushing and screening process steps are controlled.

This process produces a small quantity of emissions and is, therefore, a minor source of pollution.

Kettle Sweating Process (2). The kettle sweating process separates the metallic zinc from metal attachments, having higher melting points, and from nonmetallic residues. This is achieved by the following process steps: (a) charging the scrap into the furnace containing generally a molten heel, (b) melting of zinc fraction of the scrap, (c) working of charge to effect separation of the zinc, (d) fluxing to aid in the separation, and (e) skimming to remove impurities removed by the flux. Afterwards the molten metal may be removed and cast in blocks for further processing, fed to a distillation furnace or alloyed to obtain specification composition and then cast into ingots. Operating temperatures of the kettle-sweating baths range from 800 to 1000 F. Production is batchwise, with one batch requiring 6 to 8 hours to complete one heat.

Energy required is the electricity to drive the equipment and the fuel, generally, natural gas, to melt and keep the zinc molten. Fuel oil is used as fuel in some cases.

The process produces significant quantities of potential environmental pollutants. Atmospheric emissions consist of: (1) combustion gases (which are separate from the emissions from the molten metal), and (2) emissions consisting of gases and particulates from the molten metal. Solid wastes generated are metal attachments and skimmings or slag from the flux present in the scrap or that added to purify the zinc metal and baghouse dusts.

Composition of the particulate atmospheric emissions varies somewhat depending on the charge. However, in most cases, the emissions contain ammonium chloride, zinc, aluminum, tin, nickel, copper, iron, lead, cadmium, magnesium, manganese, and chromium. A typical analysis is shown in Table C-3. The gases are composed of, in addition to the combustion products, carbonaceous materials from the rubber, plastic, and other organic impurities or contaminants in the scrap. Some carbonaceous materials are also mixed with the particulate emissions.

Emissions factors also vary depending on the composition of the charge. When sweating metallic scrap* with zinc chloride as the flux, raw emissions factor was reported to be 10.8 lb/ton of scrap processed. These particulate emissions contained 4, 77, 4, 4, and 10 percent, respectively, of zinc chloride, zinc oxide, water, other metal chlorides and oxides, and carbonaceous materials. In other cases, the raw emissions factor for sweating residual scrap** (the flux was residual zinc chloride) was reported at 24.5 lb/ton of scrap processed. Composition of particulate emissions was similar to that from the sweating of the metallic scrap.

Morphology of the particles is dependent on the type of scrap. For example, the particle size of the emissions from sweating of residual scrap ranged from less than 1 micron to greater than 20 microns, whereas those from sweating of metallic scrap were less than 2 microns. Particle shape is acicular and/or irregular. Those emissions that are predominately zinc oxide are composed of primarily acicular particles which is the

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* Metallic scrap consists of metallic items, generally in the same shape as when manufactured or used.

** Residual scrap is composed of residues, skimmings, and other low grade scrap.

TABLE C-3. ANALYSES OF PARTICULATE EMISSIONS FROM ZINC SWEAT PROCESSING(2)

Component	Percent
$ZnCl_2$	14.5 - 15.3
ZnO	46.9 - 50.0
NH_4Cl	1.1 - 1.4
Al_2O_3	1.0 - 2.7
Fe_2O_3	0.3 - 0.6
PbO	0.2
H_2O (in $ZnCl_2 \cdot 4H_2O$)	7.7 - 8.1
Oxides of Mg, Sn, Ni, Si, Ca, Na	2.0
Carbonaceous Material	10.0
Moisture (deliquescent)	5.2 - 10.2

(2) Herring, W. O, Secondary Zinc Industry, Emission Control Problem Definition Study, Part 1, Technical Study, APCO, EPA, Durham, North Carolina.

characteristic shape of zinc oxide. Low zinc emissions have an irregular shape or are composed of a mixture of particle shapes.

Generally, the atmospheric emissions are controlled or collected using baghouses with orlon filter medium. Collection efficiencies of approximately 96 percent are reported.

No liquid wastes are generated by the kettle sweating process unless possibly some cooling water. However, significant quantities of solid wastes are generated. These wastes are: (1) slag (skimmings or drosses), (2) high melting attachments, and (3) baghouse dusts.

Thus, the kettle sweating process is a source of potential pollution problems if the wastes are not collected and disposed of properly.

Reverberatory Sweating Process (3). This process separates or recovers zinc metal from mixed zinc scrap. The recovered impure zinc is processed further to obtain specification alloys or fed to a distillation furnace for refining. The process steps are: (a) charging of furnace, (b) melting of zinc, and (c) removal of unmeltables. In this process the zinc flows from the furnace as it melts and is collected in vessels or allowed to flow to the next process in operation.

Energy required for this process is the electricity to drive the equipment and the gas or fuel oil to fire the furnace. The reverberatory furnace is direct-fired whereas the kettle furnace is heated indirectly.

Both atmospheric emissions and solid wastes are generated. The atmospheric emissions are composed of the combustion gases, gases or vapors from burning of the organic content of the scrap, and volatile metallic materials. The particulate emission is the fume volatilized from the furnace and dust carried from the furnace by the entrainment of particles in the furnace exit gases.

Composition of the atmospheric emissions varies depending on the source and type of scrap. However, in general, the particulate emission will contain such metals as zinc, aluminum, copper, iron, lead, cadmium, manganese, and chromium, in addition to carbonaceous materials and components from the residual fluxes. The gases contain primarily carbon dioxide, nitrogen, oxygen, and water, and possible sulfur oxides, chlorides, and fluorides.

Particulate emission factors vary depending on the type of scrap. For metallic scrap, raw emissions factor was reported to be approximately 13 lb of particulate matter per ton of charge processed, whereas raw emissions factor for residual scrap was reported to be approximately 32 lb per ton of feed process.(3) Baghouses with orlon filter media are used to control these emissions.(4)

Particle morphology of atmospheric emissions is the same or comparable to the morphology of emissions from the kettle furnace.

No liquid wastes are generated. Solid wastes from this process are: (1) baghouse dusts; (2) skimmings, drosses or slag; and (3) unmeltable attachments.

The process does produce significant quantities of atmospheric emissions and solid wastes which could cause pollution problems.

Rotary Sweating Process (4). Zinc metal is separated from zinc scrap such as die-castings by the rotary sweating process. During the sweating, the furnace is rotated on its axis. The zinc metal is collected in a kettle (outside the furnace) and the residue is skimmed off the molten metal.* The process steps are: (a) charging of furnace, (b) melting of zinc values, (c) removing (skimming) of residue, and (d) removing the unmeltables from the furnace. Afterwards, the impure zinc melt is transferred to a distillation furnace or alloyed and cast into ingots.

Energy required is the electrical energy to rotate the furnace and fuel (gas or oil) to heat the furance which is direct fired.

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(3) Herring, W. O., "Secondary Zinc Industry, Emissions Control Problem Definition Study, Part 1-Technical Study", NASMI, APCO, EPA, Durham, North Carolina.

(4) Air Pollution Engineering Manual, U. S. Dept. HEW NAPCA, p 307 (1967).

* No fluxes are added.

Potential environmental pollutants generated by this process are: (1) atmospheric emissions, and (2) solid wastes. The atmospheric emissions include both gases and particulate emissions. The gases are composed of those produced by combustion of the fuel and burning of organic matter contained in the scrap. The particulate emissions generally are composed of such metal values as are found in the emissions from the reverberatory sweating process. Included in this list are zinc, aluminum, copper, iron, lead, cadmium, manganese, and chromium.

Particulate emission factor data are not available. However, based on reported values from other sweating processes, it is estimated the raw emission factors will range from 11 to 25 lb of particulate matter per ton of feed.

Particulate morphology of the particles should be similar to the morphology of the particles from other sweating processes.

The solids generated by this process are skimmings, unmeltable attachments, and baghouse dusts.

The process produces significant quantities of atmospheric emissions and solid wastes and, therefore, is a potential source of atmospheric and water pollution problems.

Electric-Resistance Sweating (5). This process is employed in small plants to recover zinc from clean scrap. The process steps are: (a) charging of furnace, (b) sweating of zinc, (c) pouring of zinc melt for subsequent processing, and (d) removing residue from furnace.

Energy required is the electricity to sweat the zinc.

Potential environmental pollutants are: atmospheric emissions and solid wastes. Atmospheric emissions are composed of primarily fume and dust since only clean scrap is used as the source of zinc and no combustion products are formed. The fume and dust contain primarily zinc oxide from the oxidation of zinc vapor along with trace quantities of other heavy metals and possibly a small quantity of chloride and fluxing materials. The gaseous portion of the emissions is primarily nitrogen. Emissions are controlled with baghouses, if pollution controls are used.

Particle morphology is the same as that of emissions from other processes.

Emissions factor is probably low, <10 lb of fume and dust per ton of feed processed.

Solid wastes from this process are drosses, if fluxes are used, unmeltable components of the scrap, and baghouse dusts.

Although this process produces small quantities of atmospheric emission, there is potential atmospheric and water pollution problems associated with disposal of these materials and with the process.

Muffle Sweating Process (6). Zinc metal is recovered from zinc scrap materials by the muffle sweating process. The process steps are: (a) charging of furnace, (b) sweating of zinc values, (c) tapping of furnace to remove molten zinc for subsequent refining or alloying, and (d) removing residue with a shaker screen to separate the dross from the unmeltable attachments.

Energy required is the fuel--gas or oil--to heat the muffle furnace which is indirectly fired.

Potential pollutants from this process are: (1) atmospheric emissions composed of gases from the combustion of the fuel and from the sweating chamber and particulate emissions from the sweating chamber, and (2) solid wastes--drosses and unmeltable attachments. The gaseous emissions include those from the combustion chamber which are emitted separately to the atmosphere and those from the sweating chamber. The combustion gases contain primarily carbon dioxide, nitrogen, unburned fuel, and possibly trace quantities of heavy metals and sulfur oxides if oil is used as the source of fuel. Those from the sweating chamber are composed of a small quantity of gases from air leaking into the chamber and from combustion or decomposition of organic compounds added with the scrap.

Composition of the particulate emissions from the sweating chamber will vary depending on the type of scrap but, in general, contains the metals found in particulate emissions from other sweating processes, with the major component being zinc.

Particle morphology of the particulates is the same as that of emissions from other processes.

Emission factors for the muffle furnace process are not available. However, they are estimated to range from approximately 10.8 to 32 lb per ton of feed processed. Baghouses are used to control the emissions. A cyclone may be used in series with the baghouse.

The solid wastes generated are drosses, baghouse dusts, and unmeltable attachments.

The process generates a considerable quantity of atmospheric emissions and solid wastes, and thus is a source of pollution problems.

Sodium Carbonate Leaching Process (7). The sodium carbonate leaching process removes the nonmetallic contaminants from skimmings and residues and converts the zinc values to zinc oxide which can be reduced to zinc metal. The process steps are: (a) crushing to make the scrap more amenable to leaching, (b) washing with water to separate nonmetallic contaminants and recover metallic zinc, (c) treating the aqueous stream with sodium carbonate to precipitate the zinc values, (d) drying the precipitate to remove the water, and (e) calcining to convert zinc hydroxide to zinc oxide. The product (zinc oxide) is shipped to a primary smelter for reduction to zinc metal.

Energy required for this process is electrical energy to drive the equipment and fuel, either gas or oil, to dry and calcine the zinc hydroxide.

The process produces waste products--atmospheric emissions, liquid wastes and solid wastes--in modest quantities. The atmospheric emissions consisting of both gases and particulate matter are produced during the crushing, drying, and calcining process steps. The gases are from the crushing step and present no problem since they primarily consist of air. Those from the drying and calcining steps contain primarily the combustion gases and water vapor. Since any residual zinc chloride is vaporized during the calcination, the gases may also contain hydrogen chloride and zinc chloride. The particulate matter consists primarily of zinc oxide fume contaminated with other metal values either vaporized with the zinc oxide or entrained in the gaseous stream. The atmospheric emissions are controlled with baghouses.

Liquid wastes are generated in steps (b) and (c). These wastes contain sodium chloride, sodium carbonate, and other water-soluble compounds not precipitated by the sodium carbonate.

Because of the corrosive nature of the atmospheric emissions, allowing them to escape to the environment could cause pollution problems. Liquid wastes may cause water pollution problems if not treated before discharge.

Refining Operation

The pretreated zinc scrap still contains a wide variety of metallic and nonmetallic contaminants which are removed in the refining operation to produce pure zinc ingots, zinc dust, zinc oxide, and specification zinc alloys. These products are produced by the processes 8 through 12 as shown in the attached flowsheet entitled "Zinc Segment of the Secondary Nonferrous Metals Industry".

Retort Distillation Process (8). This process produces pure zinc ingots and pure zinc dust from pretreated zinc scrap--molten zinc-rich metal from the sweat furnace or cast zinc-rich metal ingots from a sweating process--and/or zinc dross. The process steps are: (a) charging the furnace with the pretreated zinc scrap or dross, (b) melting the charge, (c) distilling the zinc, (d) condensing the zinc vapor rapidly to produce zinc dust or slowly to produce pure liquid zinc. Afterwards, the zinc metal is removed and cast into ingots (slabs). Zinc dust, if the final product, is removed and packaged.

The energy required for this process is the fuel--gas or oil--to heat the furnace which is indirectly fired.

This process produces significant quantities of atmospheric emissions and solid wastes. Sources of atmospheric emissions are the retort opening, combustion chamber, the condenser, and casting of ingots. Emissions as zinc oxide fumes are evolved from the retort opening (charging port) during removal of the hot residue from the retort after a distillation heat and recharging of the retort for the next distillation. These emissions contain primarily zinc oxide along with aluminum, copper, and other metal values found in the residues. Raw emissions factor from this source and the condenser as discussed below are estimated to be 45 lb of particulates per ton of zinc distilled.(5) Emissions factor may be much higher due to leaks in the grout seal around the condenser neck.

Particle size of the fumes is estimated to range from approximately 0.05 to 1.0 micron. Since the fumes are primarily zinc oxide resulting from air oxidation of zinc metal, particle shape is acicular, the characteristic shape of zinc oxide.

Combustion gases which are emitted separately from the other emissions contain carbon dioxide, unburned fuel and nitrogen, and possibly trace quantities of heavy metals if oil is used as the fuel.

During distillation of zinc, the condenser must be kept positive pressure to prevent air from entering the condenser and contaminating the zinc metal with oxygen. To ensure that there is a positive pressure, a small hole, called a "speise" hole, is provided through which a small amount of zinc vapor is allowed to escape continuously into the atmosphere where it reacts with oxygen. These emissions (fumes) are essentially 100 percent zinc oxide. The particles, acicular in shape, are extremely fine, i.e., approximately 0.05 to 1 micron.

Only a small amount of atmospheric emissions is formed during the pouring and casting processing steps. Emission factors are estimated to range from 0.4 to 0.8 and 0.2 and 0.4 lb of particulates, respectively, per ton of zinc produced. These data are based on similar operations in other industries. These emissions are emitted as fine particulates with the same particle size and shape as those from the condenser.

Solid wastes generated by the retort distillation process are the distillation residues and the particulate matter, if collected, in the atmospheric emissions. The atmospheric emissions are primarily zinc oxide, whereas the distillation residues are composed of heavy metals such as residual zinc (10 to 50 percent) not removed by the distillation process and contaminants such as aluminum, copper, lead, and fluxes not removed during the pretreatment process.

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(5) Vandegriff, A. E., et al., Particulate Pollutant System Study, Volume 1-Mass Emissions, Midwest Research Institute, Kansas City, Missouri, p 179 (May 1, 1971).

In view of the quantity of atmospheric emissions and solid wastes generated by the retort distillation process, serious pollution problems may arise if the atmospheric emissions are not collected and the wastes are not disposed of by a nonpolluting method.

Muffle Distillation Process (9). This process produces pure zinc ingots, generally from pretreated zinc scrap. However, in some cases, untreated scrap such as zinc die-castings may be substituted for pretreated scrap. This process may be operated continuously whereas the retort distillation process is batch. The process steps involve: (a) continuously adding molten zinc from a melting pot or a sweating furnace to the muffle section, (b) continuously distilling and condensing the pure zinc, (c) periodically tapping the zinc from the condenser into the molds, (d) casting the zinc ingots, and (e) periodically removal of residue from muffle.

Energy utilized by this process is fuel oil or gas to supply the heat for vaporization of the zinc.

The process produces significant quantities of atmospheric emissions and solid wastes. Sources of atmospheric emissions are the combustion gases, distillation residues, pouring and casting of the ingots, and the orifice in the condenser. Emission factors, composition of emissions, and morphology of particulates are the same for both distillation processes. Atmospheric emissions may be controlled with baghouses alone or in series with cyclones.

Solid wastes generated are distillation residues and baghouse dusts which are essentially of the same composition as the solid wastes from the retort distillation process.

Thus, the process is a source of pollution problems.

Retort Distillation/Oxidation Process (10). Zinc oxide produced by the retort distillation/oxidation process involves vapor oxidation of zinc metal. The process steps in this process are the same as for the retort distillation process except zinc vapor from the retort is discharged through an orifice into a stream of air where zinc oxide is formed inside a refractory-lined chamber. The combustion gases from oxidation of the metallic zinc vapors and excess air carry the zinc oxide to a baghouse collector where the zinc oxide is collected. The combustion gases and excess air pass through the baghouse into the surrounding atmosphere.

Energy required for this process is the fuel--gas or oil--to vaporize the zinc metal.

Waste products from this process are atmospheric emissions and solid wastes. The atmospheric emissions, which consist of gases and fumes, are emitted to the atmosphere from the retort opening (charging port), baghouse, and combustion (furnace) chamber. Those from the retort opening result from oxidation of the hot residue removed after a distillation heat and upon charging of the retort with molten zinc for the next distillation heat. See the discussion on the retort distillation process for pertinent data on composition of emission, emission factors, and morphology of the particles.

Combustion gases from the retort furnace consist of primarily carbon dioxide, nitrogen, and unburned fuel. If oil is used as the fuel, the gases may also contain sulfur oxides, chlorides, and trace amounts of heavy metals.

Atmospheric emissions from the baghouse contain pure zinc oxide fume and the gases from burning of the zinc with air. The zinc oxide may contain trace quantities of heavy metals such as cadmium, depending on the purity of the feed. The particles of zinc oxide are very small, ranging in size from approximately 0.05 to about 1.0 micron. The particle shape is predominantly acicular, i.e., needle-like.

Emission factors for the baghouse are estimated at 20 to 40 lb of zinc oxide per ton of oxide produced. These data are calculated based on a collection efficiency of 98 to 99 percent.

Solid waste generated is the distillation residue remaining in the retort after removal of the zinc. This residue contains 10 to 50 percent zinc and contaminants--aluminum, copper, lead, and residual flux--not removed from the zinc scrap during the pretreatment operation.

Thus, the retort distillation/oxidation process is a source of potential environmental pollutants which can cause problems.

Muffle Distillation/Oxidation Process (11). This process produces zinc oxide from pretreated zinc scrap. The process steps are the same as for the muffle distillation process except that in the production of zinc oxide, zinc vapors are allowed to escape through an orifice at the top of the first chamber of the condenser and are burned or oxidized in the air. The resulting zinc oxide is transported by the combustion gases and excess air through conduits and collected in a baghouse.

Energy required for this process is gas or oil to heat the muffle furnace.

The potential environmental pollutants are: (1) atmospheric emissions, and (2) solid wastes. Sources of atmospheric emissions are: (1) the furnace combustion chamber which is separate from the other sources as the furnace is indirectly fired, (2) muffle opening (charging port), and (3) baghouse. See discussion on the muffle distillation process for details concerning composition of emissions, emission factors and morphology on particulates from sources (1) and (2), and the above discussion on the retort distillation/oxidation process for pertinent data on composition of emissions, emission factors, and morphology of particles for conversion of zinc to zinc oxide and subsequent collection of the zinc oxide.

Solid waste generated by the muffle distillation/oxidation process is the distillation residue from the muffle. This residue has the same composition as the residue from the retort distillation/oxidation process.

Based on these data, this process is a source of pollution problems.

Alloying Process (12). The alloying process produces zinc alloys from pretreated scrap. The process steps are: (a) melting the pretreated scrap, (b) adding the alloying agent to molten metal, (c) homogenizing the mixture, (d) pouring the melt into ingot molds, and (e) casting the ingot. In many cases, the alloying process is combined with the sweating process, whereby the molten pretreated scrap is used directly to produce the alloy.

Energy requirement for the Alloying Process is fuel--oil or gas to keep the melt molten or to melt pretreated scrap ingots.

The process produces atmospheric emissions and solid wastes. If alloying is carried out using molten zinc from a sweating furnace, the atmospheric emissions contain zinc oxide, small amounts of the alloying agent, and the flux cover. If pretreated scrap ingots are used as the source of zinc, the atmospheric emissions will contain, in addition to the particulate matter, gaseous emissions from combustion of the fuel. Particulate matter may be controlled using a baghouse; however, in many cases, no pollution control is employed.

Solid waste is the flux cover used to protect the melt. Flux covers commonly used are carbon or zinc chloride.

The process produces minor quantities of emissions and solid wastes and, therefore, is not a major source of pollution.

Graphite Rod Resistor Distillation Process (13). This process produces zinc dust from pretreated scrap ingots. The process steps are: (1) charge the ingot or melt to furnace, (2) heat with electric power, and (3) collect zinc dust as distillate using closed-loop water cooling system.

Electric energy is used in significant quantities to vaporize the zinc.

The process generates vapors containing traces of zinc, zinc oxide, lead, and lead oxide.

The pollution potential of these vapors is not significant because the metal content is recovered in baghouses and returned to the process.

The process has no pollution potential.

Population of Secondary Zinc Processors

(1) Apex Smelting Company
Division of AMAX Aluminum Company
2515 West Taylor Street
Chicago, Illinois
Telephone: (312) 332-2214

(2) Belmont Smelting and Refining Works, Inc.
320 Belmont Avenue
Brooklyn, N.Y. 11207

(3) Colonial Metals Company
Columbia, Pennsylvania
Telephone: (717) 684-2311

(4) Empire Metal Company
820 E. Water Street
Syracuse, New York 13210
Telephone: (315) 478-6950

(5) Florida Smelting Company
2640 Capitola Street
Jacksonville, Florida
Telephone: (904) 353-4317

(6) Freedman Metal Company
310 McGinnis Boulevard
Brooklyn, N.Y. 11222
Telephone: EV9-4131

(7) General Copper and Brass Company
Post Office Box 5353-D
Philadelphia, Pennsylvania
Telephone: (215) SA6-7111

(8) General Smelting Company
Division of Wabash Smelting, Inc.
2901 EW Moreland Street
Philadelphia, Pennsylvania
Telephone: GA3-3200

(9) Gettysburg Foundry
Specialties Company
Post Office Box 421
Gettysburg, Pennsylvania 17325
Telephone: 335-5616

(10) Gulf Reduction Corporation
6030 Esperson Street
Houston, Texas

(11) Holtzman Metal Company
5223 McKissock Avenue
St. Louis, Missouri 63147
Telephone: (314) CI1-3280

(12) Inland Metals Refining Co.
651 E. 119th Street
Chicago, Illinois 60628

(13) Jordan Company
Salvage Reclamation Division
5000 S. Merrimac Avenue
Chicago, Illinois 60638
Telephone: (312) PO7-6570

(14) Metchem Research, Inc.
Radcliff and Monroe Streets
Bristol, Pennsylvania
Telephone: (215) 848-0820

(15) National Metal and Smelting Company
210 NW Fourth Street
Fort Worth, Texas

(16) North American Smelting Company
Marine Terminal
Post Office Box 1952
Wilmington, Delaware
Telephone: OL4-9901

(17) Pacific Smelting Company
22219 Southwestern Avenue
Torrance, California
Telephone: SP5-3421

(18) Paragon Smelting Corporation
36-08 Review Avenue
Long Island City, N.Y. 11101
Telephone: (212) RA9-3481

(19) Roth Smelting Company
Thompson Road
Syracuse, New York

(20) George Sall Metals Company, Inc.
2255 East Butler Street
Philadelphia, Pennsylvania 19137
Telephone: (215) PI3-3900

(21) Sandoval Zinc Company
3649 South Albany Avenue
Chicago, Illinois 60632
Telephone: FR6-1900

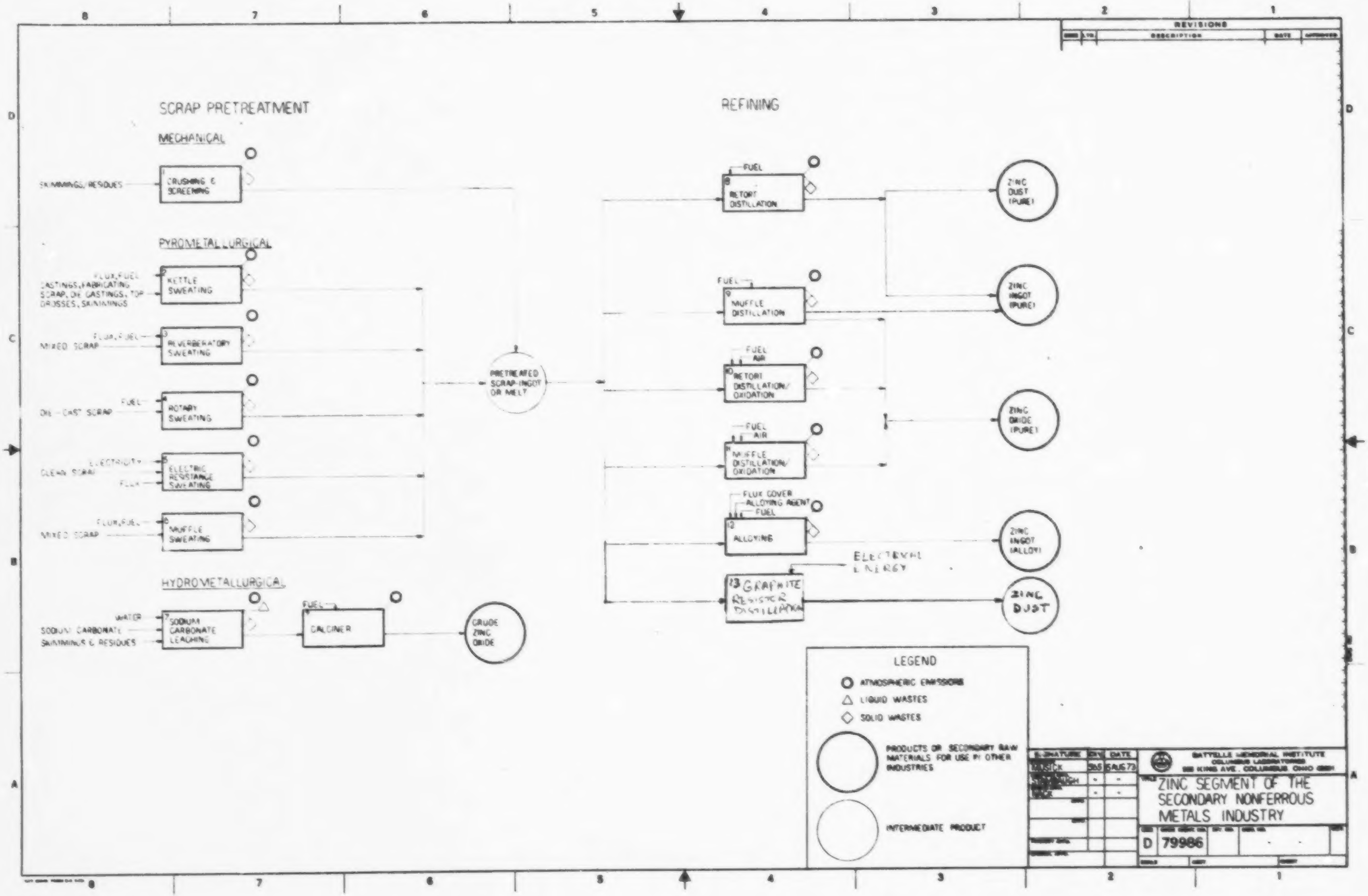
(22) SIPI Metals Corporation
1722 N. Elston Avenue
Chicago, Illinois

(23) Solken-Galamba Corporation
Second and Riverview Streets
Kansas City, Kansas 66118
Telephone: (913) MA1-4100

(24) St. Joseph Lead Company
250 Park Avenue
New York 10017
Telephone: YU6-7474

(25) U.S. Metal Products Company
Post Office Box 1067
Erie, Pennsylvania 16512
Telephone: (814) 838-2051

(26) Hyman Viener & Sons
Post Office Box 573
Richmond, Virginia 23205
Telephone: (703) 648-6563


REVISIONS
SCRAP PRETREATMENT
MECHANICAL
SKIMMINGS/RESIDUES
1 CRUSHING & SCREENING
PYROMETALLURGICAL
FLUX,FUEL
CASTINGS,FABRICATING SCRAP, DIE CASTINGS, TOP DROSSES, SKIMMINGS
2 KETTLE SWEATING
FLUX,FUEL
MIXED SCRAP
3 REVERBERATORY SWEATING
FUEL
DIE-CAST SCRAP
4 ROTARY SWEATING
ELECTRICITY
CLEAN SCRAP
FLUX
5 ELECTRIC RESISTANCE SWEATING
FLUX,FUEL
MIXED SCRAP
6 MUFFLE SWEATING
HYDROMETALLURGICAL
WATER
SODIUM CARBONATE
SKIMMINGS & RESIDUES
7 SODIUM CARBONATE LEACHING
FUEL
CALCINER
CRUDE ZINC OXIDE
PRETREATED SCRAP-INGOT OR MELT
REFINING
FUEL
8 RETORT DISTILLATION
FUEL
9 MUFFLE DISTILLATION
FUEL
AIR
10 RETORT DISTILLATION/ OXIDATION
FUEL
AIR
11 MUFFLE DISTILLATION/ OXIDATION
FLUX COVER
ALLOYING AGENT
FUEL
12 ALLOYING
ELECTRICAL ENERGY
13 GRAPHITE RESISTOR DISTILLATION
ZINC DUST (PURE)
ZINC INGOT (PURE)
ZINC OXIDE (PURE)
ZINC INGOT (ALLOY)
ZINC DUST
LEGEND
○ ATMOSPHERIC EMISSIONS
△ LIQUID WASTES
◇ SOLID WASTES
PRODUCTS OR SECONDARY RAW MATERIALS FOR USE BY OTHER INDUSTRIES
INTERMEDIATE PRODUCT
SIGNATURE
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DATE
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BATTELLE MEMORIAL INSTITUTE
COLUMBUS LABORATORIES
505 KING AVE., COLUMBUS, OHIO 43201
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